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FINAL REPORT
AN EQUATION OF STATE FOR METALS

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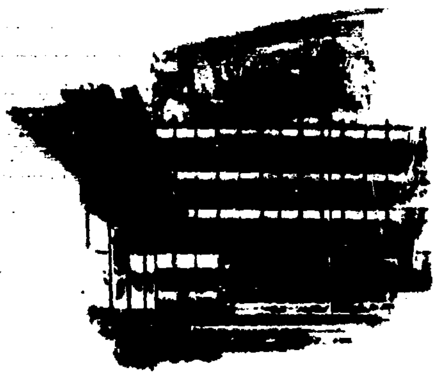

PHILCO

PHILCO-FORD CORPORATION
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Newport Beach, California

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FINAL REPORT

AN EQUATION OF STATE FOR METALS

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Washington, D.C. 20305

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ABSTRACT

An equation of state model, including the solid to liquid and liquid to vapor phase transitions, has been developed. It is applicable for materials which usually melt, rather than sublimate, and whose vapor consists of atomic species. The parameters appearing in the formulation are completely determined from a limited amount of data which, for many materials, is currently available. A computer program which gives the pressure as a function of volume and internal energy has been written and used to obtain numerical results for aluminum, titanium, and beryllium.

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LIST OF SYMBOLS

SYMBOL	MEANING
A	Constant in Raoult vapor pressure equation
A(T)	Coefficient in vapor EOS
a(t)	A(T) reduced
A'(T)	Coefficient in vapor EOS
a'(t)	A'(T) reduced
B	Constant in Raoult vapor pressure equation
B	Coefficient in vapor EOS
b	B reduced
B'	Coefficient in vapor EOS
b'	B' reduced
C	Coefficient in solid EOS
[illegible]	Specific heat at constant pressure
C_V	Specific heat at constant volume
C_ℓ	Specific heat of liquid
C_s	Specific heat of solid
$\bar{C}$	Average specific heat
c	Coefficient in reduced liquid density equation

D	Coefficient in solid EOS
d	Coefficient in reduced liquid density equation
E	Internal energy
$E_o(T)$	Internal energy of ideal gas
E_o	Internal energy of ideal gas at T = 0
$F(\mu)$	Function in solid EOS
f	Mass fraction
$G(\eta)$	Function in solid EOS
G	Coefficient in solid EOS
g_i	Multiplicity of i^{th} electronic level
H	Enthalpy
$H_o(T)$	Enthalpy of ideal gas
H_o	Enthalpy of ideal gas at T = 0
K	Bulk modulus
k	Boltzmann constant
k_o	Constant in vapor EOS
k_1	Constant in vapor EOS
k_2	Constant in vapor EOS
M	Atomic weight
N	Avagadros number
P	Pressure
p	Reduced pressure
R	Gas constant
S	Coefficient in solid EOS
T	Temperature

t	Reduced temperature
V	volume
v	Reduced volume
Z	Compressibility factor
α	Slope of reduced vapor pressure curve at the critical point
α_1	Constant in reduced vapor pressure equation
α_R	Slope of v.p. curve from Riedel formula
α_v	Volume coefficient of thermal expansion
β	Parameter in vapor EOS
Δ	Denotes a difference of quantities
ϵ	Strain
ϵ_i	Energy of i^{th} electronic level
η	ρ/ρ_o
μ	$\eta - 1$
ν	Poisson's Ratio
ρ	Density
ρ	Reduced density
σ	Stress

SUBSCRIPTS	MEANING
B	Normal boiling temperature
c	Critical value
e	Electronic contribution
ℓ	Liquid
M	Normal melting temperature

n	Normal to direction of propagation
o	Denotes zero pressure values
s	Solid
t	Translational contribution
v	Vapor

SECTION 1

INTRODUCTION

The problem of stress wave generation and propagation resulting from the deposition of a relatively large amount of energy in a very short time has been of considerable interest for over fourteen years. Various numerical techniques have been developed for solving the coupled set of hydrodynamic equations with a high-speed digital computer. Numerous versions of a one-dimensional hydrodynamic code, generally referred to as PUFF, have evolved and there has been a continuing effort to improve their capability for accurately predicting the properties of the ensuing stress wave and its effect on various materials. One objective of the DASA sponsored PREDIX Program (formerly referred to as the SUPERPUFF Program) has been to provide better input information for such a computer code.

While the basic one-dimensional hydrodynamic equations are relatively simple, the accuracy of the results of any numerical computation is no

better than that with which one can describe the energy deposition process and the equation of state for the material of interest. This report summarizes the results of an investigation pertaining to the equation of state problem.

The simplest equation of state which describes the solid phase for small strains and low energy densities is the familiar Hooke's Law with an added thermal expansion term. A more detailed equation is one which fares a modified form of this equation into the perfect gas equation at low mass densities and high energy densities. While such an equation covers the full range of densities and energies it masks all details of the solid-liquid and liquid-vapor phase transitions. More recently, an equation of state for aluminum, in tabular form, has been developed by Shock Hydrodynamics, Inc.[1,2] This equation of state is a modification of the McCloskey equation of state in which the liquid-vapor phase transition is treated in some detail. While this feature is retained in the present formulation the empirical procedures for describing the liquid phase are quite different.

The equation of state as visualized for this study is depicted in Figures 1.1a and 1.1b for a material which expands on melting. It is convenient to think in terms of the thermodynamic variables of pressure, volume, and temperature. Eventually the internal energy will be introduced to replace the temperature.

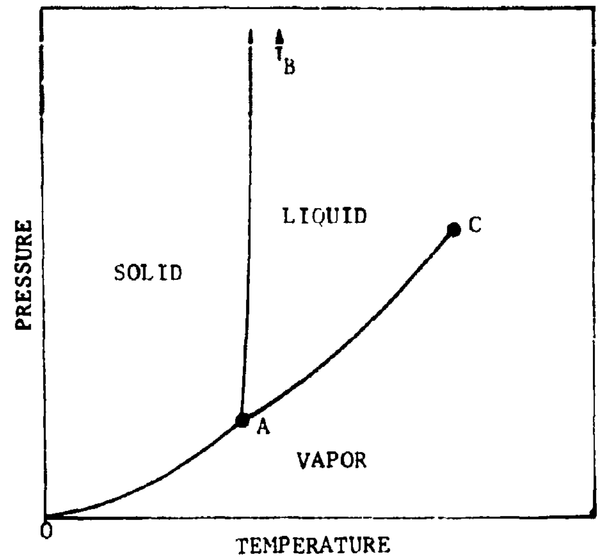

FIGURE 1.1a PHASE DIAGRAM

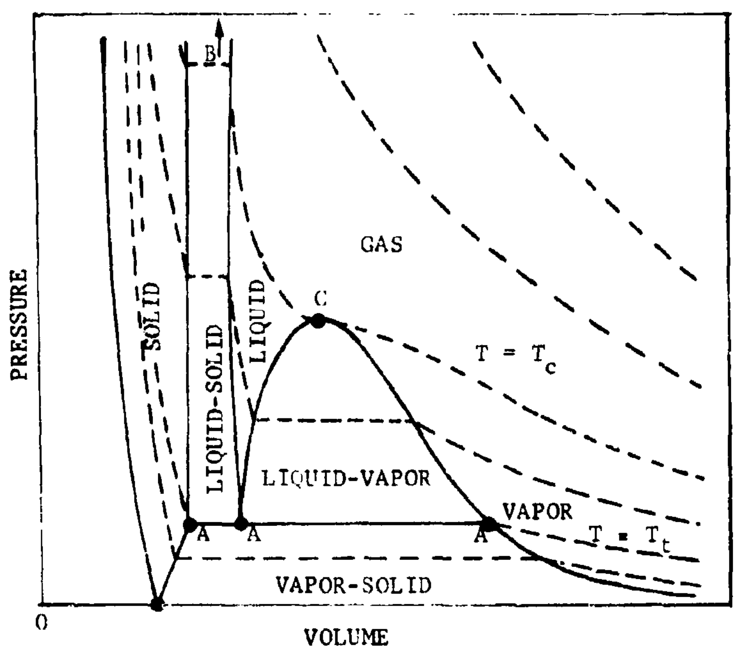

FIGURE 1.1b P-V CURVES (DASHED LINES) FOR THE MATERIAL OF FIGURE 1.1a

FIGURES 1.1 EQUATION OF STATE FOR A MATERIAL WHICH EXPANDS UPON MELTING

A P-T phase diagram showing the solid, liquid, and vapor phases separated by lines along which phase transitions occur is shown in Figure 1.1a. Point C is the critical point represented by the critical pressure P_c, critical volume V_c, and critical temperature T_c, while point A is the triple point where all three phases can exist in equilibrium. The phase transition lines become mixed phase regions in the P-V diagram of Figure 1.1b. One might expect the solid-liquid region to have a top, as does the liquid-vapor region, but none has ever been observed.

An equation of state as shown in Figure 1.1 is an equilibrium situation and hence equilibrium is assumed throughout. Rate effects can be included in the equation of state for the solid phase without affecting the rest of the development. Furthermore, the pressure of Figure 1.1 is a hydrostatic pressure, equal in all directions. For one-dimensional stress wave propagation in materials which can support shears the stress normal to the direction of propagation is different from that in the direction of propagation. This problem, which arises only in the solid phase, will be considered at the appropriate time.

The equation of state depicted in Figure 1.1 does not allow for negative pressures in the solid phase, and the solid sublimates at sufficiently low pressure. For the materials considered, however, the available data indicates that the triple point pressure, if a triple point exists, is many orders of magnitude below one atmosphere. Hence it is assumed that the pressure at point A can be taken as zero and therefore the sublimation region is neglected. Furthermore, the melting line AB is extremely steep

so the temperature at point A can be taken equal to the normal melting temperature. The resulting modified equation of state is shown in Figure 1.2. Negative pressures in the solid phase are now possible for temperatures less than the normal melting temperature or for internal energies less than that at which the material begins to melt. This simplification does not apply, of course, to materials like carbon which normally sublimate.

The problem then is to determine parameters for the equation of state of Figure 1.2 for materials of interest. Unfortunately, the amount of data for most materials is quite limited and one is forced to make numerous assumptions. An attempt is made, however, to keep the formulation somewhat flexible so that any additional data which might become available can be included to refine the parameters.

Section 2 summarizes the available data, not only for the materials considered in the study, but also for other materials where experimental measurements around the critical point have been made. This enables one to retain certain qualitative features of an equation of state where data is known but also indicates marked differences between different types of materials.

The bulk of the effort is contained in Section 3 where analytical expressions for various regions of the PV diagram are developed. The liquid phase is the most difficult to describe and the procedure taken is to approach it both from the vapor phase through the vapor-liquid transition region and from the solid phase through the solid-liquid transition region. In

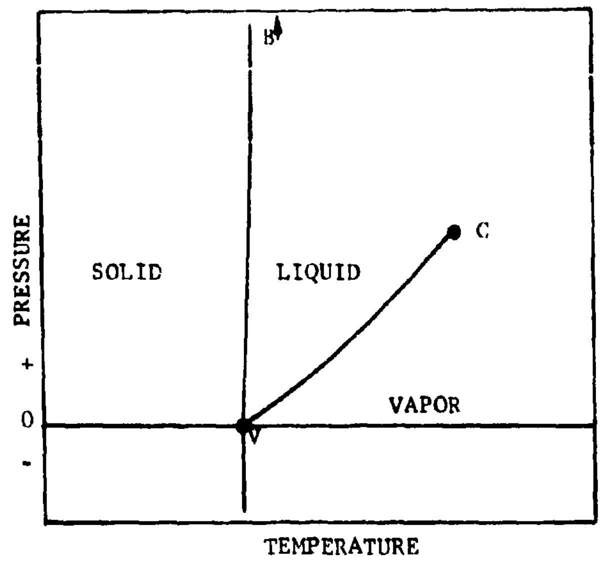

FIGURE 1.2a MODIFIED PHASE DIAGRAM

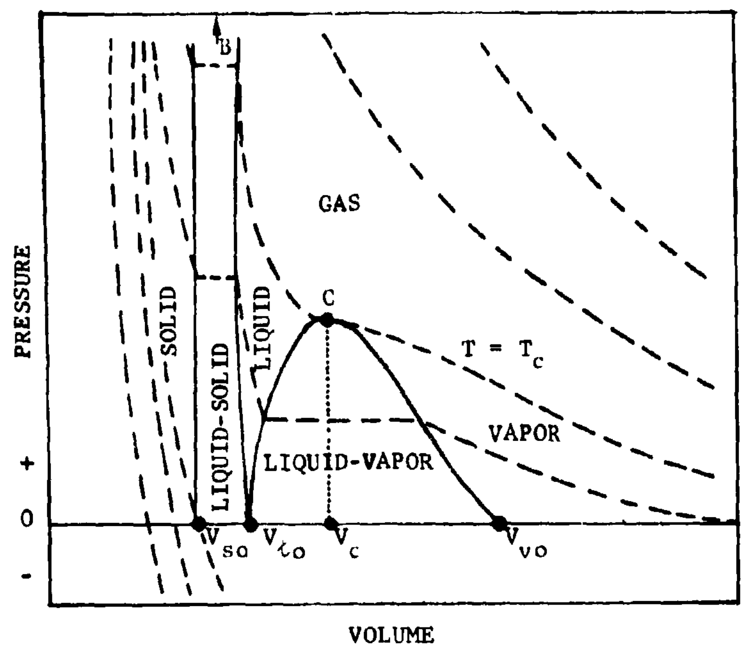

FIGURE 1.2b MODIFIED P-V CURVES (DASHED LINES) FOR THE MATERIAL OF FIGURE 1.2a

FIGURE 1.2 MODIFIED EQUATION OF STATE FOR A MATERIAL WHICH EXPANDS UPON MELTING

the process of developing the analytical expressions, a possible procedure for determining the necessary parameters from a limited amount of data is outlined.

Section 4 describes an equation of state subroutine which, given a volume V and an energy E, determines the pressure P. An initial calculation determines the required parameters from relatively simple input data.

The results of some calculations using this subroutine are given in Section 5 for aluminum, titanium and beryllium. Isoenergy curves and adiabats have been determined to check out the subroutine.

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SECTION 2

DATA

The amount of data for various materials is quite extensive for those which are vapors under normal conditions or become vapors at very low temperatures, rather complete for materials such as mercury and the alkali metals which vaporize at reasonable temperatures, and very limited for metals whose boiling temperatures are quite high. This section summarizes some of the data which is useful as a guideline in the subsequent development. The more pertinent data is plotted in Figures 2.1 and 2.2.

2.1 MATERIALS WITH LOW BOILING TEMPERATURES

The data for materials which are vapors under normal conditions and those which boil at very low temperatures have been analyzed in detail by Hirschfelder, et. al.[3,4,5] These include the noble gases, hydrocarbons, and the highly polar substances, water and ammonia. Data exists for rather wide ranges of temperature, density, and pressure both below and above the critical point values. The result of the analysis is a generalized

equation of state, containing relatively few parameters, for the vapor, liquid, and mixed phases.

An important parameter which appears throughout is the critical compressibility factor Z_c defined by

$$Z_c \equiv P_c V_c / R T_c \tag{2.1}$$

where P_c, V_c, and T_c are the critical pressure, molar volume, and temperature, respectively. R is the molar gas constant. Typical values of Z_c for these materials are:

Substance	Z_c
Noble gases	0.29-0.30
Light hydrocarbons	0.27
Water	0.23

While substances which vaporize at high temperatures do not fall into the same regime as those analyzed by Hirschfelder, et. al, several of the analytical forms proposed by them have been retained to describe the vapor phase and the liquid-vapor mixed phase.

2.2 MERCURY

Data on the thermodynamic properties of mercury are more complete and probably more accurate than for any other metal. Measurements of the vapor pressure[6,7] and the saturated liquid and vapor densities[8] have been made to very near the critical point. On the basis of these data, the critical parameters are estimated[9] to be

$T_c = 1733\ ^oK$ $\qquad$ $P_c = 1587$ atm

$\rho_c = 4.7$ gm/cc $\qquad$ $Z_c = 0.48$

By assuming a principle of corresponding states, that the vaporization entropy of various liquids is equal at corresponding temperatures, Grosse[9] also estimates the critical temperatures for other materials. This idea is retained, but some weight is also given to the data for the alkali metals.

2.3 ALKALI METALS

The vapor pressures of the alkali metals have been measured up to 100 psi[10] and the data in this low temperature, low pressure range can be fit with a Raoult relation of the form

$$\log P = A - B/T. \qquad (2.2)$$

The constants A and B are given in Table 2.1, when the temperature is in degrees Kelvin and the pressure is in atmospheres.

Table 2.1: Vapor Pressure Constants for the Alkali Metals

Element	A	B
Na	4.52172	5220.42
K	4.09537	4205.78
Rb	4.04261	3880.020
Cs	3.941504	3702.814

Dillon, et. al.[11] have measured the saturation densities of both liquid and vapor up to near the critical point and from this data they estimate the critical properties of the alkali metals. The critical parameters

are listed in Table 2.2.

Table 2.2: Critical Parameters for the Alkali Metals.

Element	Atomic Weight	Boiling Temp. (^oK)	Critical Temp. (^oK)	Critical Density (gm/cc)	Critical Press.[a] (atm)	Compressibility Factor
Na	22.99	1183	2573 $\pm$ 350	0.206 $\pm$ 0.041	350	0.20 $\pm$ 0.12
K	39.10	1039	2223 $\pm$ 330	0.194 $\pm$ 0.037	160	0.21 $\pm$ 0.13
Rb	85.47	974	2093 $\pm$ 35	0.346 $\pm$ 0.009	157	0.22 $\pm$ 0.02
Cs	132.90	958	2057 $\pm$ 40	0.428 $\pm$ 0.012	145	0.25 $\pm$ 0.02

[a]Estimated Error $\pm$ 20%.

The values shown were taken from their table and there is no explanation for slight discrepancies which appear. In the following it is assumed that the critical temperatures and densities are correct.

This data can now be used to construct curves of vaporization entropy as a function of the reduced temperature, $t = T/T_c$, at least for the lower temperatures, in the following manner. The Clapeyron equation for the slope of the vapor pressure curve is

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_v - V_\ell)} \tag{2.3}$$

where ΔH is the latent molar heat of vaporization at the temperature T and pressure P, V_v is the molar volume of the saturated vapor, and V_ℓ is the molar volume of the saturated liquid. At low temperatures, $V_v >> V_\ell$, and it is further assumed that V_v is that for an ideal gas. Hence

$$V_v - V_\ell \approx V_v \approx RT/P. \tag{2.4}$$

The vaporization entropy is then

$$\frac{\Delta H}{T} \approx \frac{RT}{P}\frac{dP}{dT} \approx RT\ (2.3026\ \frac{B}{T^2}) = 2.3026\ \frac{RB}{T} = 2.3026\ \frac{RB}{T_c}\ \frac{1}{t} \qquad (2.5)$$

where use has been made of Eq. (2.2) to evaluate the derivative. This function is plotted in Figure 2.1, using the values of B and T_c from Tables 2.1 and 2.2. Also shown in Figure 2.1 are experimental values for Hg[9] and a range of values[9] for the low boiling temperature substances. This figure will be used to estimate the critical temperatures for other metals.

Another quantity of interest is the reduced saturated liquid density as a function of the reduced temperature. This is plotted in Figure 2.2. In addition to the alkali metal data, some Hg data points and a range of values for hydrocarbons are also shown. Hirschfelder[3] suggests that the data for a given material can be fit with the empirical form

$$\rho_\ell = 1 + c\ (1-t)^{1/3} + d\ (1-t), \qquad (2.6)$$

where ρ_ℓ is the reduced density and t is the reduced temperature. The alkali metal data can all be fit with the same curve with c = 1.8 and d = 1.75. This function is also shown in Figure 2.2.

2.4 ALUMINUM, TITANIUM AND BERYLLIUM

There is no direct data available at high temperatures and pressures for aluminum, titanium and beryllium. This information must be derived from other data which is at hand. Table 2.3 indicates the type of information which is usually available for the metals and lists values for the three metals being considered.

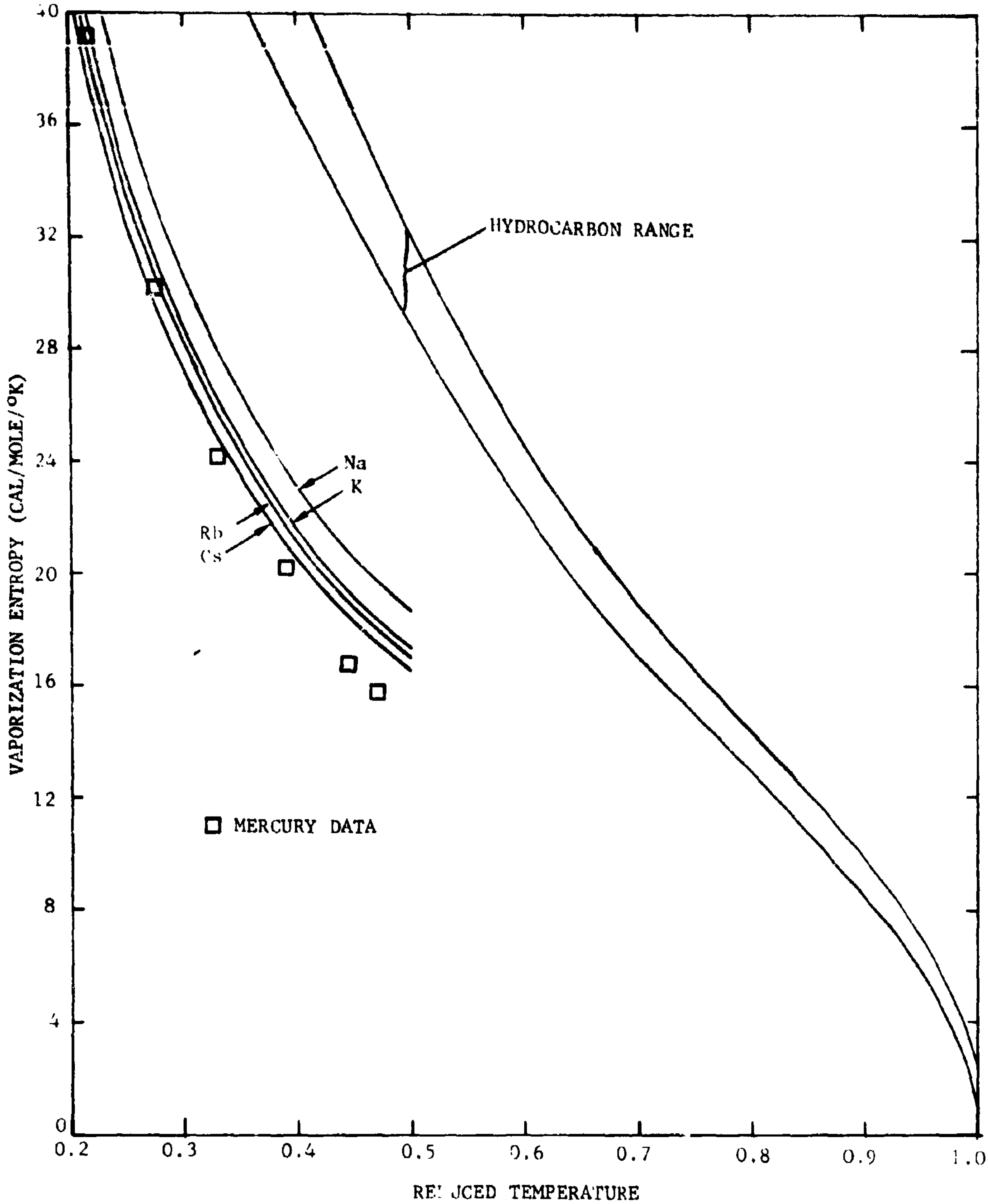


FIGURE 2.1 VAPORIZATION ENTROPY VERSUS REDUCED TEMPERATURE

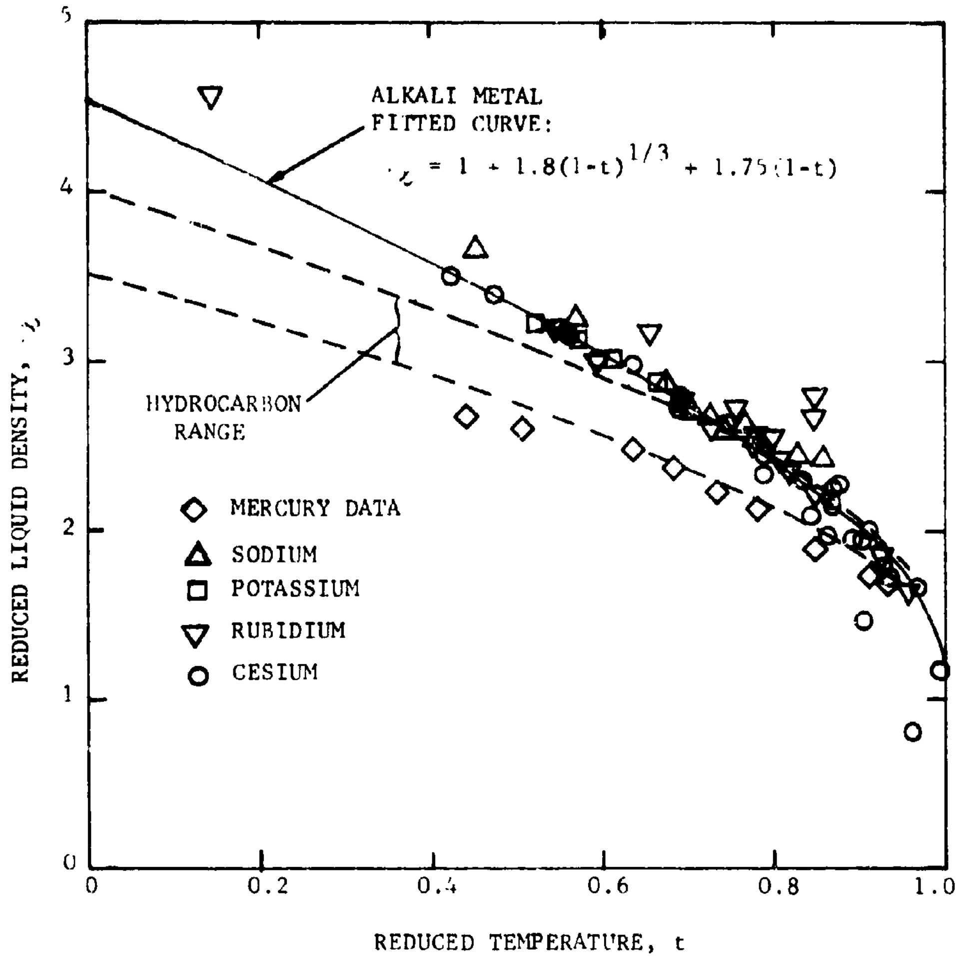


FIGURE 2.2 REDUCED LIQUID DENSITY VERSUS REDUCED TEMPERATURE

Table 2.3. Data for Aluminum, Titanium and Beryllium

Metal	Aluminum	Titanium	Beryllium
Atomic Weight (gm/mole)	26.98	47.90	9.013
Solid:			
Normal Density (gm/cc)	2.71	4.5	1.85
C (kbar)[12]	772.0	1016	1203
D (kbar)[12]	490.8	722.2	821.2
S (kbar)[12]	607.6	-568.5	-379.0
C (kbar/cal/gm)[12]	0.2384	0.2044	0.08938
Poisson's Ratio	1/3		
Solid to Liquid:			
Melting Temperature (^{o}K)[13]	932	1950	1556
Solid Enthalpy (kcal/mole)[13]	4.291	13.390	7.910
Liquid Enthalpy (kcal/mole)[13]	6.838	17.094	10.714
Vapor Enthalpy (kcal/mole)[13]	81.177	121.274	84.504
Heat of Fusion (kcal/mole)	2.547	3.704	2.798
Solid Density (gm/cc)	2.537[14]	(4.25)	1.808[15] (1.73)
Liquid Density (gm/cc)	2.380[14]	(3.97)	1.690[15] (1.62)
Slope of PT Curve (atm/^{o}K)	161	[illegible]	213 (210)
Liquid to Vapor:			
Boiling Temperature (^{o}K)[13]	2736	3550	2757
Liquid Enthalpy (kcal/mole)[13]	19.466	29.894	19.342
Vapor Enthalpy (kcal/mole)[13]	90.149	132.348	90.477
Heat of Vaporization (kcal/mole)	70.683	102.454	71.135
Liquid Density (gm/cc)	1.92 (2.07)	(3.65)	1.551[15] (1.47)
Vaporization Entropy (cal/mole/^{o}K)	25.83	28.86	25.80

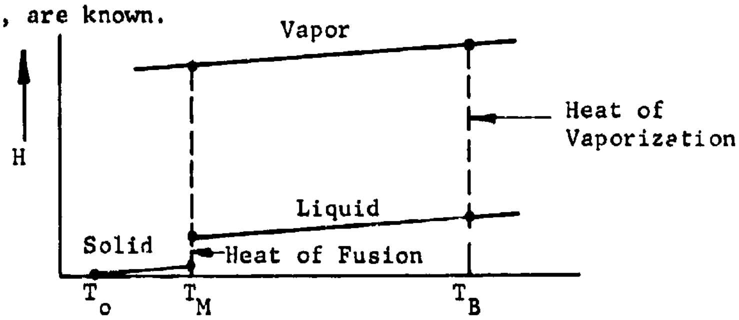
It is assumed that an analytical form of the equation of state for the solid exists, i.e., pressure as a function of density ρ and internal energy E. Various forms have been proposed but, for the purpose of this discussion, it is taken to be[12]

$$P(\rho, E) = C\mu + D\mu^2 + S\mu^3 + G\,\eta\,E. \qquad (2.7)$$

$\eta = \rho/\rho_o$, ρ_o being the normal density, and $\mu = \eta - 1$. The internal energy is referenced relative to normal density and room temperature. The values for the coefficients were taken from the RADS report.[12] Analytical forms different from that given in Eq. (2.7) can be handled with no more difficulty by making minor changes in the computer program described later.

For many metals there is a solid phase change and this should be included in the solid equation of state. In this case it is necessary to have an expression for the material at high internal energies, around the energy at which it begins to melt, in order to describe the melting process.

The solid-to-liquid and liquid-to-vapor phase transitions are described by values of certain thermodynamic quantities at the normal melting temperature and normal boiling temperature, respectively. In particular, it is assumed that the values of the enthalpy at these temperatures, as indicated in the following diagram, are known.



This is just the information that one has frequently used to arrive at a total energy of vaporization. The enthalpy values listed in Table 2.3 were taken from the JANAF Tables.[13]

In some cases values of the solid and liquid densities at the melting temperature have been measured. If so, they can be used as input data. There is, however, a consistency condition that the solid equation of state evaluated at the solid density and the energy at which the solid begins to melt yield zero pressure.

In the case of aluminum, the solid density has been assumed to be correct requiring the internal energy at the melting temperature to be increased by 1.44 kcal/mole (53.52 cal/gm). All other internal energies are increased accordingly, retaining the indicated heats of fusion and vaporization which are taken to be correct.

For titanium, these densities have not been measured and hence it has been assumed that the solid internal energy at the melting temperature (equal to the enthalpy since the pressure is taken to be zero) is correct. The solid density is then found to be 4.25 gm/cc, given in parenthesis. The liquid density has been taken equal to 6.5% less than the solid density. This is consistent with the density decrease for other materials where data is available.

Beryllium is unique in that at a temperature of 1250°C the crystal structure changes from a hcp to a bcc form with a corresponding increase in density of 4.8%.[15] The hcp form has a density of 1.725 gm/cc while the bcc form

has a density of 1.808. This accounts for the relatively high solid density given in the table. If this density is used, the solid internal energy must be decreased by 5.142 kcal/mole (570.5 cal/gm). The value of 1.73 gm/cc, given in parenthesis, is obtained by assuming the solid internal energy is correct. The liquid density is again taken to be 6.5% less than the solid density. There are discrepancies of about 4.3% in the two sets of values.

The slope of the P-T melting curve can be evaluated from the Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_\ell - V_s)} , \qquad (2.8)$$

where ΔH, the heat of fusion, is equal to the difference in the liquid and solid enthalpies. Calculated values for this slope are given in Table 2.3. Note that they are extremely steep ($\sim$ 100-200 atm/$^{\circ}$K). Hence, going from one atmosphere pressure to zero pressure changes the melting temperature by less than a hundredth of a degree and the melting temperature values given are certainly valid at zero pressure.

The liquid density at the boiling temperature is known for some materials, or can be estimated by extrapolating liquid density data above the melting temperature. This information has not been used, however, and the values given in parenthesis are those obtained by the procedure to be outlined later. In the case of aluminum the discrepancy is about 8%, but then the density value of 1.92 gm/cc is highly questionable. It is less for beryllium.

Values for the vaporization entropy, equal to the heat of vaporization divided by the boiling temperature, are also given.

At this point the critical temperatures can be estimated. It is assumed that, for the metals, the vaporization entropies at the normal boiling temperatures fall in the range defined by the alkali metals. Hence, from Figure 2.1, reasonable values of the critical temperatures are $8000^{\circ}K$, $11{,}600^{\circ}K$, and $8000^{\circ}K$ for aluminum, titanium, and beryllium, respectively. This procedure effectively says that the critical temperature for a metal is proportional to its heat of vaporization at the boiling temperature and an approximate formula is

$$T_c\ (^{\circ}K) \approx 113\ \Delta H_B\ (\text{kcal/mole}). \tag{2.9}$$

If one side or the other of the alkali range is chosen, instead of the center, the critical temperatures can vary by $\pm\ 500^{\circ}K$ from the above values.

The lack of high temperature data makes it difficult to check the assumptions made in developing an equation of state formulation. Appendix A describes a laser deposition, inertial confinement, experiment, suggested by the qualitative results of this study, which might provide some of this high temperature information.

SECTION 3

EQUATION OF STATE

This section suggests various analytical forms for the thermodynamic variables in different regions of the phase diagram. As has already been mentioned, the liquid region seems to be the most difficult to treat. The procedure adopted is to approach it both from the vapor phase at very low densities and from the solid phase at nearly normal densities. In view of the lack of data, it is necessary to make numerous assumptions. The formulation which is developed should be refined to incorporate any new data.

2.1 VAPOR PHASE

The general formulation of Hirschfelder, et. al.,[3,4,5] for describing the vapor phases of the noble gases and hydrocarbons is retained. In this formulation the proposed equation of state for the vapor is a generalization of the van der Waals equation and can be written

$$(P + A(T)/V^2 + A'(T)/V^3)\ (V-B+B'/V) = RT. \tag{3.1}$$

Hence, van der Waals' constant A, related to the energy of attraction between molecules, is replaced by $A(T) + A'(T)/V$, a function of both temperature and volume, and the constant B, related to the excluded volume occupied by the molecules, is replaced by $B - B'/V$, B and B' being constants.

It is convenient to write Eq. (3.1) in terms of reduced variables, $p = P/P_c$, $v = V/V_c$, and $t = T/T_c$ by dividing by

$$P_c V_c = Z_c RT_c. \tag{3.2}$$

Then

$$(p + a(t)v^2 + a'(t)/v^3)(v-b+b'/v) = \frac{1}{Z_c} t \tag{3.3}$$

where

$$a(t) = A(T)/P_c V_c^{\,2},\ a'(t) = A'(T)/P_c V_c^{\,3},\ b = B/V_c,\ b' = B'/V_c^2. \tag{3.4}$$

Eq. (3.3) can be solved for p in terms of t and the reduced density, $\rho = 1/v$,

$$p = \rho t/Z_c(1-b\rho + b'\rho^2) - a(t)\rho^2 - a'(t)\rho^3. \tag{3.5}$$

A connection between the various parameters of Eq. (3.5) is obtained by the requirement that the first and second partial derivaties of p with respect to ρ vanish at the critical point, $p = \rho = t = 1$. Assuming for the moment that $a'(1) = 0$, this gives

$$\begin{aligned} a(1) &= \beta \\ b &= (3\beta^2 - 6\beta - 1)/\beta\,(3\beta - 1) \\ b' &= (\beta - 3)/(3\beta - 1). \end{aligned} \tag{3.6a}$$

where β is a new parameter introduced for convenience and uniquely related to Z_c by

$$Z_c = P_c V_c / RT_c = \beta(3\beta - 1)/(\beta + 1)^3. \tag{3.6b}$$

$\beta = 3$, $Z_c = 0.375$, $a = 3$, $b = 1/3$, $b' = 0$, with $a' = 0$, corresponds to the original van der Waals equation.

It should be noted here that Eq. (3.6b) indicates a maximum value for Z_c of 0.3790 occurring when $\beta = 2.535$. Hence there is this restriction in using the form of Eq. (3.1). Typical values of β as a function of Z_c are given in Table 3.1.

Table 3.1: Parameter β as a Function of Z_c.

Z_c	β	Z_c	β
0.23	9.24	0.28	6.71
0.24	8.65	0.29	6.30
0.25	8.12	0.30	5.90
0.26	7.62	0.31	5.52
0.27	7.15	0.32	5.51

The temperature dependent forms suggested for $a(t)$ and $a'(t)$ are

$$\begin{aligned} a(t) &= k_o + (\beta - k_o)/t = k_o + k_1/t \\ a'(t) &= \frac{1}{2}(1 - k_o + 2\beta - \alpha)(t - 1/t) = k_2(t - 1/t). \end{aligned} \tag{3.7}$$

k_o is an adjustable constant and Hirschfelder, et. al. use the value of 5.5 throughout their calculations. They point out, however, that a value of 4.71 might give a better fit to the noble gases and hydrocarbon data.

Since typical Z_c values for the metals seem to be around 0.31, and since a better value for k_o is not known, it has arbitrarily been taken equal to β for obtaining the results of Section 5. α is a parameter discussed in the next section and, for the present, it is sufficient to note that $\partial p/\partial t$ evaluated at the critical point is equal to α.

The internal energy E in the vapor phase can be derived from the thermodynamic relationship

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{3.8}$$

In terms of reduced variables this differential equation becomes

$$\left(\frac{\partial E}{\partial v}\right)_t = Z_c RT_c \left[t\left(\frac{\partial p}{\partial t}\right)_v - p\right]. \tag{3.9}$$

The internal energy is now found by integrating along an isotherm from infinite volume or zero density,

$$\begin{aligned} E(v \text{ or } \rho, t) - E_o(T) &= Z_c RT_c \int_\infty^v \left[t\left(\frac{\partial p}{\partial t}\right)_v - p\right] dv \\ &= Z_c RT_c \int_o^\rho \left[p - t\left(\frac{\partial p}{\partial t}\right)_\rho\right] \frac{d\rho}{\rho^2} = Z_c RT_c \left[-(k_o + 2k_1/t)\rho + k_2\, \rho^2/t\right] \end{aligned} \tag{3.10}$$

$E_o(T)$ is the internal energy of the completely separated molecules at the temperature in question and an analytical expression for it is required.

For the present it is assumed that the vapor at zero density is an ideal monatomic gas and that there are only translational and electronic contributions to the internal energy. The contribution due to translation is quite simple and

$$E_t(T) = \frac{3}{2} RT. \tag{3.11}$$

There is also a contribution from electronic excitation at the higher temperatures and this is given by

$$E_e(T) = N \frac{\sum_i g_i \epsilon_i e^{-\frac{\epsilon_i}{kT}}}{\sum_i g_i e^{-\frac{\epsilon_i}{kT}}} \qquad (3.12)$$

g_i is the statistical weight of the i^{th} energy level, or group of levels with approximately the same energy, and ϵ_i is the corresponding energy. This internal energy contribution is for one mole when N = 6.02338 x 10^{23}/ mole, Avagadro's number. Energy conversion factors are required to give specific units for the internal energy. A set of multiplicities and electronic levels for aluminum are given in Table 3.2.

Table 3.2. Multiplicities and Electronic Levels for Aluminum.

g_i	ϵ_i(ev)	ϵ_i(^{o}K)	g_i	ϵ_i(ev)	ϵ_i(^{o}K)
2	0	0	6	4.9932	57950
4	0.0139	161	14	5.1226	59452
2	3.1426	36472	12	5.2319	60719
12	3.6078	41870	20	5.4054	62734
16	4.0541	47050	18	5.0583	63928
2	4.6726	54229	84	5.7191	66374
10	4.8265	56014	LIMIT	5.9855	69466

The internal energy for an ideal monatomic gas is then

$$E_o(T) = E_o + E_t\ (T) + E_e(T) \qquad (3.13)$$

where E_o is a reference energy at $0\ ^oK$. This is eventually chosen to give zero internal energy for the solid at normal density and room temperature.

In principle Eqs. (3.11)-(3.13) could be used to determine the internal energy for an ideal gas. It is rather complicated and, in view of other uncertainties in the formulation, it seems that a simplified expression might suffice. There are various possibilities but the one used assumes that the enthalpy of an ideal gas can be approximated by a linear function of the temperature whose slope is determined by the enthalpies at the melting and boiling temperatures. Hence

$$H_o(T) = H_o + C_P T \qquad (3.14)$$

where the effective specific heat is

$$C_P = \frac{H_V(T_B) - H_V(T_M)}{T_B - T_M} \qquad (3.15)$$

The expression for the internal energy of an ideal gas is then

$$E_o(T) = H_o(T) - RT = E_o + C_V T \qquad (3.16)$$

where $C_V = C_P - R$. From the enthalpy values of Table 2.3, C_V values are 2.99, 4.93, and 2.99 cal/mole/^oK for aluminum, titanium, and beryllium respectively. One advantage of this linear form is that Eq. (3.10) can be solved for t once E and ρ are given.

Eqs. (3.5), (3.10), and (3.16) now represent the equation of state for the vapor phase giving pressure and internal energy as functions of the density and temperature. They are used up to the vapor-liquid mixed phase envelope for $t < 1$ and up to the critical density for $t > 1$.

2.2 VAPOR-LIQUID MIXED PHASE.

In order to describe the vapor-liquid mixed phase region, it is necessary to have an expression for the vapor pressure as a function of the temperature. Over a rather limited range of temperatures the Raoult relation has frequently been used and the vapor pressure equation is of the form

$$\ell n\ P = A - B/T. \tag{3.17}$$

While this form may be sufficiently good, a somewhat more general form has been adopted.

A starting point for developing this more general form is the Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_v - V_\ell)}, \tag{3.18}$$

where the subscripts v and ℓ refer to the vapor and liquid phases respectively. ΔH is the heat of vaporization at the temperature T. At the lower temperatures the vapor volume is much larger than the liquid volume and nearly given by that for an ideal gas. Hence

$$V_v = V_\ell \approx V_v \approx RT/P. \tag{3.19}$$

Furthermore the heat of vaporization at these low temperatures is approximately given by

$$\Delta H \approx \Delta H_B + \Delta C\ (T - T_B), \tag{3.20}$$

where ΔC is the difference in specific heats at constant pressure for the vapor and liquid and the subscript B denotes the normal boiling temperature. To the same approximation used in the previous section the vapor

specific heat is given by Eq. (3.15) and the liquid specific heat is given by

$$C_\ell = \frac{H_\ell\ (T_B) - H_\ell\ (T_M)}{T_B - T_M} \tag{3.21}$$

Eqs. (3.19) and (3.20) make it possible to integrate Eq. (3.18) with the result that

$$\ell n\ \frac{P}{P_B} = \frac{\Delta H_B - \Delta C T_B}{R} \left[\frac{1}{T_B} - \frac{1}{T}\right] + \frac{\Delta C}{R}\ \ell n\ \frac{T}{T_B}. \tag{3.22}$$

Ideally P_B, the pressure at the normal boiling temperature T_B, is one atmosphere but this condition is relaxed somewhat.

It is convenient to express Eq. (3.22) in terms of reduced variables and then it can be written

$$\ell n\ p = (\alpha - \alpha_1)\ (1 - 1/t) + \alpha_1\ \ell n\ t, \tag{3.23}$$

where α and α_1 are dimensionless parameters defined by

$$\alpha = \frac{\Delta H_B + \Delta C\ (T_c - T_B)}{RT_c},\ \alpha_1 = \frac{\Delta C}{R}. \tag{3.24}$$

Eq. (3.23) is now assumed to hold throughout the temperature range $t \leq 1$ with α and α_1 given by Eq. (3.24). α is the same quantity appearing in Eq. (3.7) and it is the slope of the reduced vapor pressure curve evaluated at the critical point. Using the critical temperatures deduced in Section 2.4, values of α for aluminum, titanium and beryllium are 3.78, 4.08 and 3.74, respectively.

In principle, one could assume a normal boiling pressure of one atmosphere and, knowing a critical temperature, determine the critical pressure from

Eq. (3.22). There is the possibility of considerable error in doing this, however, due to the rapid variation of pressure with temperature and the uncertainty in the vapor pressure curve around the critical point. Therefore an alternative approach which first determines the less sensitive parameter Z_c has been used.

Hirschfelder, et. al., use a form for the reduced vapor pressure suggested by Riedel,

$$\ell n\ p = \alpha_R\ \ell n\ t - 0.0838\ (\alpha_R - 3.75)\ \left(\frac{36}{t} - 35 - t^6 + 42\ \ell n\ t\right). \quad (3.25)$$

α_R is the slope of this vapor pressure curve at the critical point and is the only parameter appearing. Hence, if one used this form he would be inclined to choose α_R to satisfy the Clapeyron equation at the boiling temperature. Eq. (3.19) is valid here and hence

$$\frac{1}{p}\frac{dp}{dt}\bigg|_{t=t_B} = \frac{\Delta H_B}{RT_c}\ \frac{1}{t_B^2} \quad (3.26)$$

determines α_R. In addition to Eq. (3.25), Riedel suggests a relationship between α_R and the critical compressibility factor Z_c given by

$$Z_c = \left[3.72 + 0.26\ (\alpha_R - 7\right]^{-1}. \quad (3.27)$$

While this procedure for determining Z_c is questionable, since Eqs. (3.25) and (3.27) are based on hydrocarbon data, it does give reasonable values around 0.307 for the three metals being considered.

The vapor side of the vaporization envelope is now determined by setting the equation for the pressure of the vapor, Eq. (3.5), equal to the vapor

pressure, Eq. (3.23), and solving for the vapor density ρ_v as a function of $t < 1$,

$$\rho_v t/Z_c(1-b\rho_v+b'\rho_v^2) - a'(t)\rho_v^2 - a(t)\rho_v^3 = \exp\left[(\alpha-\alpha_1)(1-1/t) + \alpha_1 \ln t\right] \quad (3.28)$$

In this equation, all variables are reduced. There is always a solution since the form of the equation for the pressure of the vapor was chosen such that $\partial p/\partial t = \alpha$ at the critical point. This ensures that, for a given $t < 1$, the vapor pressure is less than the first peak in the modified van der Waals equation for the pressure of the vapor. The internal energy $E_v(t)$ along this envelope is then found from Eq. (3.10).

The liquid side of the vaporization envelope must be determined independently and the form suggested by Hirschfelder, et. al., is retained for doing this. This assumes that the reduced liquid density ρ_ℓ can be adequately represented by

$$\rho_\ell(t) = 1 + c(1-t)^{1/3} + d\,(1-t) \quad (3.29)$$

where c and d are constants for a particular material. The internal energy along the liquid side of the envelope is determined from its value on the vapor side and the Clapeyron equation, Eq. (3.18). In terms of reduced variables,

$$\frac{dp(t)}{dt} = \frac{1}{Z_c RT_c}\,\frac{H_v-H_\ell}{t(v_v-v_\ell)} = \frac{1}{Z_c\,RT_c}\left[\frac{E_v - E_\ell}{t(v_v-v_\ell)} + \frac{p}{t}\right], \quad (3.30)$$

and

$$E_\ell(t) = E_v(t) - Z_c\,RT_c(v_v-v_\ell)t\left[\frac{dp(t)}{dt} - \frac{p}{t}\right] \quad (3.31)$$

$$= E_v(t) - Z_c RT_c\,(v_v-v_\ell)\,p(t)\left[(\alpha-\alpha_1)/t + \alpha_1 - 1\right]$$

Hence, the internal energy, pressure, and density are known on the liquid side of the saturation envelope.

In the vapor-liquid mixed phase region it is convenient to introduce the vapor mass fraction f and then volume V, internal energy E, and f are related through the temperature t by

$$V = f\ V_v\ (t) + (1 - f)\ V_\ell(t) \qquad (3.32a)$$

$$E = f\ E_v(t) + (1-f)\ E_\ell(t) \qquad (3.32b)$$

In general one wishes to determine P(V,E) and the coupled set of equations for doing this are Eqs. (3.10) (with Eq. (3.16)), (3.23), (3.28), (3.29), (3.31), (3.32a), and (3.32b). These equations involve the 7 variables t, $p(t)$, $v_v(t)$, $v_\ell(t)$, $f(t)$, $E_v(t)$, and $E_\ell(t)$.

Two of the critical parameters, ρ_c and P_c, remain undetermined. In the overall equation of state as visualized, Figure 1.2, it is necessary to join the vapor-liquid and solid-liquid mixed phase regions at zero pressure. Doing this serves to determine the critical density ρ_c. Eq. (3.29) evaluated at the reduced melting temperature is

$$\rho_\ell\ (T_M) = \rho_c \left[1 + c\ (1 - t_M)^{1/3} + d\ (1 - t_M) \right], \qquad (3.33)$$

where the densities here are actual densities, and this can be solved for ρ_c. c and d are not generally known for the metals and in all numerical work it has been assumed that the values c = 1.8, d = 1.75, appropriate for the alkali metals, also apply for aluminum, titanium and beryllium. This gives critical densities of 0.557, 0.958, 0.396 gm/cc, respectively.

The beryllium value of 0.396 corresponds to the liquid density value of 1.62 from Table 2.3. The critical pressures are now found from

$$P_c = Z_c \; RT_c/V_c. \tag{3.34}$$

Table 3.3 summarizes the set of critical parameters which have been determined for the three metals considered.

Table 3.3: Critical Parameters for Aluminum, Titanium and Beryllium

Metal	Aluminum	Titanium	Beryllium
Temperature (^{o}K)	8000	11600	8000
Density (gm/cc)	0.5569	0.9580	0.3964
Pressure (kbar)	4.161	5.846	8.857
Compressibility Factor (Z_c)	0.3071	0.3071	0.3067
Slope of V.P. Curve (α)	3.775	4.068	3.745
Parameter α_1	-1.020	-0.5428	-1.112
Parameter β	5.626	5.626	5.638

It should be noted that the formulation as described doesn't give exactly zero pressure at the melting temperature. Values obtained are 6.0×10^{-12}, 1.9×10^{-6}, and 1.0×10^{-4} atm for aluminum, titanium and beryllium, respectively. Although negligible, these values have been subtracted from the calculated pressures in the vapor phase and the vapor-liquid mixed phase to ensure zero pressure on the axis. Furthermore, the vaporization envelope now terminates at a very large but finite volume rather than tailing off to an infinite volume.

The problem of determining the critical pressure from the vapor pressure equation has already been mentioned and by following the procedure described, the so-called boiling temperatures, instead of corresponding to one atmosphere, occur at pressures of 1.2, 0.32, and 2.8 atm for aluminum, titanium and beryllium, respectively. The boiling temperatures at one atmosphere are now 2694°K (2736), 3852°K (3550), and 2553°K (2757).

2.3 SOLID PHASE

An equation of state for the solid phase is presumably known and that which is required for the following formulation is an equation valid around energies where melt begins. The effect of any change in crystalline structure in the solid phase is a separate problem which should be included in specifying the solid equation of state. Also, in the idealized one-dimensional propagation problem, the stress in a direction normal to the direction of propagation is different from that in the direction of propagation. This is briefly considered in Appendix B. For the following, however, it is assumed that an expression for the hydrostatic pressure, valid at the higher energies, is known.

Various forms for the solid equation of state have been used and, in general, they are of the form

$$P(\rho,E) = C\mu + F(\mu) + G(\eta)\ E, \tag{3.35}$$

where $\eta = \rho/\rho_o$ and $\mu = \eta - 1$. The particular form assumed for the purpose of making calculations is

$$P(\rho,E) = C\mu + D\mu^2 + S\mu^3 + G\,\eta\,E \tag{3.36}$$

with C, D, S and G being constants for a particular material. Values for aluminum, titanium and beryllium are given in Table 2.3.

A polynomial form for $F(\mu)$ is usually adequate for fitting the data around normal densities but the condition that the pressure be a monotonically increasing function of the density is often violated. This occurs both for titanium and beryllium where the constant S has negative values. Hence the $P - \rho$ isoenergy curve passes through a maximum at a relatively high density and this poses a problem for the proposed formulation. Alternatives are to alter the solid equation of state so it is monotonically increasing function of the density or to modify the formulation. This problem is considered again in the next section.

As has already been mentioned, there is the condition that the solid denity and energy at which the material begins to melt at zero pressure must be compatible with Eq. (3.35). They cannot be independently specified and the suggested procedure is to specify one of them and calculate the other. Discrepancies introduced by doing this are usually not large. These quantities will be designated by ρ_{so} and E_{so}.

2.4 SOLID-LIQUID MIXED PHASE

The only condition which must be strictly adhered to in describing the solid to liquid phase transition is the Clapeyron equation which, in this case, is

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_\ell - V_s)} \quad . \tag{3.37}$$

ΔH is now the heat of fusion, in general a function of the temperature, and subscripts s and ℓ refer to the solid and liquid phases respectively. In order to define the mixed phase region further, it is necessary to make several assumptions.

It was pointed out in Section 2.4 that, at the normal melting temperature, the slope of the transition curve is quite large, 100 to 200 atm/^{o}K, for the metals considered. It probably becomes larger at higher temperatures but the assumption is made that it remain constant and equal to its value at zero pressure. Hence, the equation for the solid to liquid transition curve is

$$P = \frac{\Delta H_M}{V_{\ell o} - V_{so}} \left[\frac{T}{T_M} - 1 \right] \equiv \frac{\Delta E_o}{\Delta V_o} \left[\frac{T}{T_M} - 1 \right] \qquad (3.38)$$

$V_{\ell o}$ is the liquid volume, at the zero pressure melting temperature, which is either specified or can be estimated as some reasonable fraction like 6.5% larger than the solid volume. The volume difference on melting is denoted by ΔV_o. The heat of fusion at zero pressure is $\Delta H_M = H_\ell(T_M) - H_s(T_M)$ and this is also equal to the internal energy difference denoted by ΔE_o.

A direct consequence of this assumption is obtained from Eqs. (3.37) and (3.38), with $H = E + PV$, and

$$\frac{\Delta E}{\Delta V} \equiv \frac{E_\ell(T) - E_s(T)}{V_\ell(T) - V_s(T)} = \frac{\Delta E_o}{\Delta V_o} \quad . \qquad (3.39)$$

In other words, the ratio of the energy difference to the volume difference between the liquid and solid at the temperature T is independent of the temperature.

It has been observed that, at least for the lower temperatures near the normal melting temperature, both the melting entropy $\Delta H(T)/T$ and the volume change $\Delta V(T)$ are nearly constant.[16] Hence, assuming Eq. (3.39) is correct, the internal energy difference $\Delta E(T)$ is also nearly constant.

The initial slopes of both the solid and liquid internal energies are presumably known, since they are just the respective specific heats. From the type of data available the specific heat of the solid can be determined from

$$C_s = \frac{H_s\ (T_M)}{T_M - 298} \tag{3.40}$$

and that for the liquid is given by Eq. (3.21). It is now assumed that the average internal energy for the solid and liquid is linear in the temperature with a slope given by the average specific heat at T_M. Hence,

$$\bar{E}(t) = \frac{E_\ell(T) + E_s(T)}{2} = \frac{E_\ell(T_M) + E_s(T_M)}{2} + \bar{C}\ (T-T_M). \tag{3.41}$$

Suggested forms for the individual energies are

$$E_\ell(T) = E_{\ell o} + \bar{C}(T-T_M) + \frac{\Delta C}{2} T_M \left[\frac{T_M}{T} - 1 \right] , \tag{3.42}$$

$$E_s(T) = E_{so} + \bar{C}(T-T_M) - \frac{\Delta C}{2} T_M \left[\frac{T_M}{T} - 1 \right] , \tag{3.43}$$

where ΔC is the difference in specific heats at T_M. Each internal energy starts out with the right slope and becomes linear in temperature at large temperatures. In general ΔC is quite small and hence the internal energy difference doesn't change much for these assumed forms. Similarly ΔV doesn't change much and the melting entropy is nearly constant.

The density for the solid on the melting curve is obtained by equating Eqs. (3.35) and (3.38) at the temperature T,

$$P_s(\rho_s(T),\ E_s(T)) = P(T). \tag{3.44}$$

In the melting region the volume V and internal energy E are related through the liquid fraction f by

$$V = f\ V_\ell + (1-f)V_s, \tag{3.45a}$$

$$E = f\ E_\ell + (1-f)\ E_s. \tag{3.45b}$$

All quantities on the right of these equations are functions of the temperature T.

The coupled set of equations for finding P(V,E) in this mixed phase region are now Eqs. (3.38), (3.39), (3.42), (3.43), (3.44), (3.45a), and (3.45b), involving the 7 variables T, P(T), $V_s(T)$, $V_\ell(T)$, f(T), $E_s(T)$, and $E_\ell(T)$. Again, the simplest iterative procedure converges rather rapidly.

Qualitatively, this formulation has the effect of bending the transition region toward higher densities at the higher pressures. One result of this is that a phase transition can occur at normal density for energies somewhat higher than the zero pressure values and rather high pressures. This is illustrated in Table 3.4.

Table 3.4: Normal Density Melting Energies and Pressures

Metal	Aluminum	Titanium	Beryllium
Energy at Zero Pressure (cal/gm)	213	280	878
Energy at Normal Density (cal/gm)	340	427	1360
Pressure at Normal Density (kbar)	81	87	120
Temperature at Normal Density ($^{\circ}K$)	1440	2820	2170

In Section 3.2 the reference energy for the vapor was undetermined and it is now chosen so that the liquid energy is equal to $E_{\ell 0}$, all energies being referenced to zero energy for the solid at normal density and zero pressure.

Pushing this model still further, to higher densities, pressures, and energies, requires that the solid equation of state be assumed correct under these extreme conditions. In doing this the problem mentioned in the last section arises and if the solid isoenergy curve is not a monotonically increasing function of the density one eventually reaches a situation where Eq. (3.43) no longer has a solution. This limitation is probably not serious for the solid phase and the solid-liquid mixed phase, where the densities are not expected to be too large, but it does prevent one from determining the boundary of the liquid phase for high energies.

Aside from this problem, the proposed model completely describes the solid-liquid transition region and, in particular, fixes the pressure, density and energy on the liquid side of this region.

2.5 LIQUID PHASE

As has been mentioned, the liquid phase seems to be the most difficult phase to describe. In principle, the equation of state formulation developed to this point defines the boundaries of the liquid phase region and determines the thermodynamic variables on these boundaries. Any assumption made for bridging the gap is highly questionable, however.

A possible approach is to construct isotherms through the liquid region and find the energies along the isotherms from Eq. (3.8). The proposed formulation, however, determines the energies at the end points, along the liquid sides of the mixed phase regions, and obtaining agreement by this approach may be rather formidable. Since the quantity of primary interest is internal energy, a simpler procedure is to develop empirical expressions for curves along which it is constant.

Various expressions have been considered and, since the choice is somewhat arbitrary, there is a tendency toward simplicity as long as the results are "reasonable."

One simple expression assumes that the pressure is a linear function of the density for a given energy. Hence, denoting this pressure by $P_1(\rho,E)$,

$$P_1(\rho,E) = \frac{P_{\ell M} - P_{\ell B}}{\rho_{\ell M} - \rho_{\ell B}}\,\rho - \frac{\rho_{\ell B}\,P_{\ell M} - \rho_{\ell M}\,P_{\ell B}}{\rho_{\ell M} - \rho_{\ell B}} , \qquad (3.46)$$

where the subscripts M and B denote the melting and boiling sides of the liquid region, respectively. All subscripted variables are functions of the energy E. For energies greater than that at the critical point,

$\rho_{\ell B} = \rho_c$ and $P_{\ell B} > P_c$. Pressures obtained with this equation seem quite high, particularly at the higher energies.

A second simple expression results from taking the logarithm of the pressure as a linear function of the logarithm of the density. Denoting this pressure by $P_2(\rho, E)$,

$$\ell n\ P_2(\rho, E) = \frac{\ell n\ (P_{\ell M}/P_{\ell B})}{\ell n\ (\rho_{\ell M}/\rho_{\ell B})}\ \ell n\ \rho - \frac{\ell n\ \rho_{\ell B}\ \ell n\ P_{\ell M} - \ell n\ \rho_{\ell M}\ \ell n\ P_{\ell B}}{\ell n\ (\rho_{\ell M}/\rho_{\ell B})} \quad (3.47)$$

This gives rather reasonable pressures for the higher energies but leads to a crossing of curves of constant energy for the lower energies. In fact, the curve may cut down through the melting region.

A third expression, and the one included in the equation of state program, is obtained by taking a linear combination of the logarithms of the presures P_1 and P_2. Hence

$$\ell n\ P\ (\rho, E) = F(E)\ \ell n\ P_1(\rho, E) + (1 - F(E))\ \ell n\ P_2\ (\rho, E) \quad (3.48)$$

where F(E) is somewhat arbitrary. Reasonable results have been obtained by limiting it to the range 0 to 1 and determining it from the condition that

$$\left.\frac{\partial P(\rho, E)}{\partial \rho}\right|_{\rho_{\ell M}} = \frac{P_{\ell M}\ (E)}{\rho_{\ell M}(E) - \rho_{\ell o}} \quad (3.49)$$

By choosing it this way, the curves of constant energy do not cross and, in general, Eq. (3.46) is predominant at low energies while Eq. (3.46) determines the pressure at high energies.

SECTION 4

EQUATION OF STATE SUBROUTINE

An equation of state subroutine for finding the pressure P for a given volume V and internal energy E, according to the formulation described in the previous section, has been programmed and checked by using it in two, rather simple, main programs. It has not been tested in a PUFF hydrodynamic program. In writing this program the emphasis was placed on obtaining a workable program rather than on efficiency and hence, there is undoubtedly room for improvement. A listing of the subroutine is given in Appendix C.

The required input information is given in Table 4.1. The equations which are solved are scattered throughout Section 3 with justification for the assumed forms. They are assembled here for clarity. The density ρ and volume V are both used, depending on which is more convenient, and one is just the reciprocal of the other. In some instances the reduced values are also used. A consistent set of units is implied.

Table 4.1: Input Information for Equation of State Subroutine.

Description	Units	Notation: Formulation	Notation: Subroutine
Atomic Weight	gm/mole	M	WT
Normal Density	gm/cc	ρ_o	DO
Critical Temperature	^oK	T_c	TCK
Coefficient in Liquid Density Equation	None	c	C1
Coefficient in Liquid Density Equation	None	d	D1
Parameter in Vapor EOS[(a)]	None	k_o	KO
Melting Temperature	^oK	T_M	TMK
Solid Enthalpy at T_M	kcal/mole	$H_s(T_M)$	HSM
Liquid Enthalpy at T_M	kcal/mole	$H_\ell(T_M)$	HLM
Vapor Enthalpy at T_M	kcal/mole	$H_v(T_M)$	HVM
Solid Density at T_M[(b)]	gm/cc	$\rho_s(T_M)$	DSM
Liquid Density at T_M[(c)]	gm/cc	$\rho_\ell(T_M)$	DLM
Boiling Temperature	^oK	T_B	TBK
Liquid Enthalpy at T_B	kcal/mole	$H_\ell(T_B)$	HLB
Vapor Enthalpy at T_B	kcal/mole	$H_v(T_B)$	HVB
Coefficient in Solid EOS[(d)]	kbar	C	C
Coefficient in Solid EOS[(d)]	kbar	D	D
Coefficient in Solid EOS[(d)]	kbar	S	S
Coefficient in Solid EOS[(d)]	kbar/cal/gm	G	G
Zero (Make initial calculations)	None		INIT

Legend for Table 4.1.

a. If this is zero, it is set equal to 3.

b. If this is zero, it is determined from the solid EOS with $E = H_s(T_M)$ If a value is specified the corresponding energy is determined from the solid EOS and all other energies are renormalized.

c. If this is zero, it is taken to be 6.5% less than the solid density.

d. The solid EOS is assumed to be of the form given in Eq. (3.36).

Figure 4.1 shows the various regions in a P-V diagram and defines certain quantities useful in specifying the boundaries of these regions. The complete set of equations is as follows:

<u>Pressure Calculations</u>

<u>Solid Phase</u>: $\eta = \rho/\rho_o$, $\mu = \eta - 1$.

$$P_s(\rho,E) = C\mu + D\mu^2 + S\mu^3 + G\eta E. \qquad (4.1)$$

Determine $P = P_s(\rho,E)$

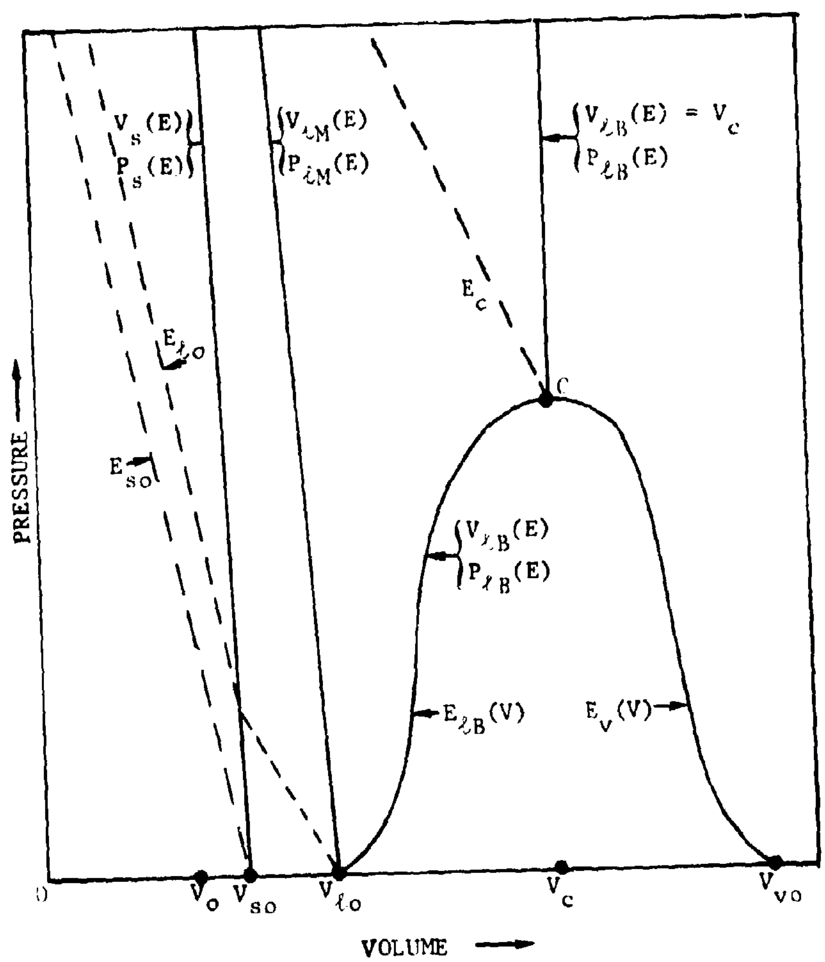


FIGURE 4.1 P-V PHASE DIAGRAM DEFINING THE VARIOUS REGIONS

Solid-Liquid Mixed Phase:

$$P(T) = \Delta E_o/\Delta V_o(T/T_M - 1) \tag{4.2a}$$

$$P_s(\rho_s(T), E_s(T)) = P(T) \tag{4.2b}$$

$$\frac{E_\ell(T) - E_s(T)}{V_\ell(T) - V_s(T)} = \frac{\Delta E_o}{\Delta V_o} \tag{4.2c}$$

$$E_\ell(T) = E_{\ell o} + \bar{C}\, T_M(T/T_M - 1) - \frac{\Delta C\, T_M}{2}(T_M/T - 1) \tag{4.2d}$$

$$E_s(T) = E_{so} + \bar{C}\, T_M(T/T_M - 1) + \frac{\Delta C\, T_M}{2}(T_M/T - 1) \tag{4.2e}$$

$$V = f_\ell(T)\, V_\ell(T) + \left[1 - f_\ell(T)\right] V_s(T) \tag{4.2f}$$

$$E = f_\ell(T)\, E_\ell(T) + \left[1 - f_\ell(T)\right] E_s(T) \tag{4.2g}$$

Determine T, V_ℓ, V_s, E_ℓ, E_s, f_ℓ, $P = P(T)$.

Liquid Phase:

$$P_1(\rho,E) = \frac{P_{\ell M} - P_{\ell B}}{\rho_{\ell M} - \rho_{\ell B}}\,\rho - \frac{\rho_{\ell B} P_{\ell M} - \rho_{\ell M} P_{\ell B}}{\rho_{\ell M} - \rho_{\ell B}} \tag{4.3a}$$

$$\equiv A(E)\rho - B(E)$$

$$\ell n\, P_2(\rho,E) = \frac{\ell n\,(P_{\ell M}/P_{\ell B})}{\ell n\,(\rho_{\ell M}/\rho_{\ell B})}\,\ell n\,\rho - \frac{\ell n\,\rho_{\ell B}\,\ell n\,P_{\ell M} - \ell n\,\rho_{\ell M}\,\ell n\,P_{\ell B}}{\ell n\,(\rho_{\ell M}/\rho_{\ell B})} \tag{4.3b}$$

$$= C(E)\,\ell n\,\rho - D(E)$$

$$F(E) = \left[\frac{P_{\ell M}}{\rho_{\ell M}} C(E) - \frac{P_{\ell M}}{\rho_{\ell M} - \rho_{\ell o}} \right] / \left[\frac{P_{\ell M}}{\rho_{\ell M}} C(E) - A(E) \right] \quad (4.3c)$$

$$\ell n\, P_{\ell}\, (\rho, E) = F(E)\, \ell n\, P_1(\rho, E) + \left[1 - F(E) \right] \ell n\, P_2(\rho, E) \quad (4.4d)$$

Determine $P = P_{\ell}(\rho, E)$

Liquid-Vapor Mixed Phase: (Reduced densities)

$$p(t) = \exp \left[(\alpha - \alpha_1)(1 - 1/t) + \alpha_1\, \ell n\, t \right] \quad (4.4a)$$

$$p_v(\rho_v(t), t) = p(t) \text{ determines } \rho_v(t) \quad (4.4b)$$

$$\rho_{\ell}(t) = 1 + c\, (1-t)^{1/3} + d(1-t) \quad (4.4c)$$

$$E_v(t) = E_o + C_v T_c t - Z_c R T_c \left[(k_o + 2k_1/t)\, \rho_v(t) - k_2\, \rho_v^2(t)/t \right] \quad (4.4d)$$

$$E_{\ell}(t) = E_v(t) - Z_c R T_c \left[v_v(t) - v_{\ell}(t) \right] p\,(t) \left[(\alpha - \alpha_1)/t + \alpha_1 - 1 \right] \quad (4.4e)$$

$$V = f_v(t)\, V_v(t) + \left[1 - f_v(t) \right] V_{\ell}(t) \quad (4.f)$$

$$E = f_v(t)\, E_v(t) + \left[1 - f_v\, (t) \right] E_{\ell}(t) \quad (4.4g)$$

Determine t, v_v, v_{ℓ}, E_v, E_{ℓ}, f_v $P(V,E) = P_c \left[p(t) - p_{vo} \right]$

Vapor-Phase: (Reduced density)

$$p_v(\rho, t) = \rho t / Z_c (1 - b\rho + b' \rho^2) - (k_o + k_1/t)\, \rho^2 - k_2 (t - 1/t) \rho^3 \quad (4.5a)$$

$$E = E_o + C_v T_c t - Z_c RT_c \left[(k_o + 2k_1/t)\,\rho - k_2\,\rho^2/t \right] \qquad (4.5b)$$

Determine t, $P = P_c \left[p_v(\rho, t) - p_{vo} \right]$.

<u>Calculations of Boundary Variables</u>

<u>Solid-Liquid Mixed Phase Region</u>:

$E_{so} < E$

Solve Eqs. (4.2a), (4.2b) and (4.2e) with $E_s = E$, for $V_s(E) = V_s(T)$.

$E_{so} < E < E_{\ell o}$

$$V_{max}(E) \equiv \left[(E - E_{so})\, V_{\ell o} + (E_{\ell o} - E)\, V_{so} \right] \Big/ (E_{\ell o} - E_{so})$$

If $V > V_{max}(E)$, $P \equiv 0$.

$E_{\ell o} < E$

Solve Eqs. (4.2a)-(4.2e) with $E_\ell = E$, for $V_{\ell M}(E) = V_\ell(T)$, $P_{\ell M}(E) = P(T)$.

<u>Liquid-Vapor Mixed Phase Region</u>:

$E_{\ell o} < E < E_c$

Solve Eqs. (4.4a)-(4.4e) with $E_\ell = E$, for $V_{\ell B}(E) = V_c/\rho_\ell(t)$, $P_{\ell B}(E) = P_c \left[p(t) - p_{vo} \right]$.

$E_{\ell o} < E < E_{vo}$

$$V_{max}(E) = \left[(E-E_{\ell o})\,V_{vo} + (E_{vo} - E)V_{\ell o}\right] / (E_{vo}-E_{\ell o})$$

If $V > V_{max}(E)$, $P = 0$.

$E_c < E$

$V_{\ell B}(E) = V_c$. Solve Eqs. (4.5a) and (4.5b), with $\rho = 1$,

for $P_{\ell B}(E) = P_c\left[p_v(1,t) - p_{vo}\right]$

$V_{\ell o} < V < V_c$

Solve Eqs. (4.4a)-(4.4e), with $\rho_\ell = V_c/V$, for $E_{\ell B}(V) = E_\ell(t)$.

$V_c < V < V_{vo}$

Solve Eqs. (4.4a), (4.4b), and (4.4d), with $\rho_v = V_c/V$, for

$E_v(V) = E_v(t)$.

<u>Calculations of Equation of State Parameters.</u>

If $\rho_s(T_M) \le 0$; $E_{so} = H_s(T_M)$, $P_s(\rho_{so}, E_{so}) = 0$ determines ρ_{so}.

> 0; $\rho_{so} = \rho_s(T_M)$, $P_s(\rho_{so}, E_{so}) = 0$ determines E_{so}.

$E_{\ell o} = E_{so} + H_\ell(T_M) - H_s(T_M)$

If $\rho_\ell(T_M) \le 0$; $\rho_{\ell o} = 0.935\,\rho_{so}$. (A different fraction could be used.)

> 0; $\rho_{\ell o} = \rho_\ell(T_M)$

$$\rho_c = \rho_{\ell o}\left[1 + c\,(1-t_M)^{1/3} + d\,(1-t_M)\right]$$

$\Delta H_B = H_v(T_B) - H_\ell(T_B)$

$\alpha_R + 0.0838\ (\alpha_R - 3.75)\ (36/t_B + 6t_B^6 - 42) = \Delta H_B / RT_c\ t_B$ determines α_R

$Z_c = \left[3.72 + 0.26\ (\alpha_R - 7)\right]^{-1}$

$P_c = Z_c R T_c\ \rho_c / M$

$C_P = \left[H_V(T_B) - H_V(T_M)\right] / (T_B - T_M)$, $C_V = C_P - R$

$C_\ell = \left[H_\ell(T_B) - H_\ell(T_M)\right] / (T_B - T_M)$

$\Delta C = C_P - C_\ell$

$\alpha = \left[\Delta H_B + \Delta C\ (T_c - T_B)\right] / RT_c$, $\quad \alpha_1 = \Delta C / R$

$Z_c = \beta(3\beta - 1)/(\beta + 1)^3$ determines β

$b = (3\beta^2 - 6\beta - 1)/\beta(3\beta - 1)$, $\quad b' = (\beta - 3)/(3\beta - 1)$

If $k_o = 0$, $k_o = \beta$. If $k_o \neq 0$, $k_o = k_o$.

$k_1 = \beta - k_o$, $\quad k_2 = \frac{1}{2}(1 - k_o + 2\beta - \alpha)$

Let $E_o = H_v(T_B) - C_P\ T_B = E_o'$

Solve Eqs. (4.3a)-(4.3e), with $t = t_M$, for $\rho_{vo} = \rho_c\ \rho_\ell(t)$, $p_{vo} = p(t)$

$E_o = E_o' + \left[E_{\ell o} - E_\ell(t)\right]$, $E_{vo} = (E_o - E_o') + E_v(t)$.

This renormalization of energy assures that $E_{\ell o} = E_{\ell}(t_M)$

$$E_c = E_o + C_V T_c - Z_c R T_c \left[k_o + 2k_1 - k_2 \right]$$

$$\Delta E_o = E_{\ell o} - E_{so}$$

$$\Delta V_o = V_{\ell o} - V_{so}$$

$$C_s = H_s (T_M)/(T_M - 298)$$

In essence the subroutine does three things:

1.) The first time through it calculates the critical parameters, and other parameters appearing in the equations, from a limited amount of input information. (This is only done once and these calculations could be placed in the main program.)

2.) It calculates the necessary boundaries of the various regions of the phase diagram for the given values of the energy E and volume V.

3). It determines which phase or mixed-phase region the values of the volume and energy fall in and calculates the pressure accordingly.

The checking starts with the solid phase and works toward the vapor phase. Hence a minimum amount of time is wasted in determining a pressure in the solid phase.

As written, the subroutine gives the pressure in kbar for the volume in cc/gm and the energy in cal/gm. This is obtained by the statement

$$\text{"Pressure"} = P(\text{"Volume"}, \text{"Energy"}) \tag{4.1}$$

where any designation for "Pressure", "Volume", and "Energy" in the main program may be used.

The explicit form for the solid equation of state given by Eq. (4.1) has been considered but the more general form of Eq. (3.35) only requires reprogramming the functions $F(\mu)$, $G(\eta)$, and their derivatives. These are designated by FF(MU), GG(ETA), FFP(MU), and GGP(ETA) respectively. Corresponding changes must also be made in the input.

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SECTION 5

NUMERICAL RESULTS

The equation of state subroutine described in Section 4 and listed in Appendix C has been used in two programs for the purposes of checking it out and obtaining some numerical results for aluminum, titanium, and beryllium. In the process of doing this, certain parameters appearing in the formulation were extracted. These are given in Table 5.1. The critical constants for aluminum from Ref. 2 are $T_c = 6000^{\circ}K$, $\rho_c = 0.590$ gm/cc, $P_c = 3.11$ kbar, and $Z_c = 0.292$. In view of the lack of data, the differences are probably not significant.

Figures 5.1 - 5.3 show curves of constant energy for aluminum, titanium, and beryllium, respectively. The $\ln P$ vs $\ln \rho$ plots best show the details of the liquid-vapor mixed phase and the vapor phase where the pressures and densities are relatively low.

The high pressure, high density region for aluminum is shown in Figure 5.4. On this plot the liquid-vapor mixed phase is completely lost. In addition

Table 5.1. Calculated Equation of State Parameters

Metal	Aluminum	Titanium	Beryllium
Critical Parameters:			
Temperature (^{o}K)	8000	11600	8000
Density (gm/cc)	0.5569	0.9580	0.3964
Pressure (kbar)	4.161	5.846	8.857
Compressibility Factor (Z_c)	0.3071	0.3071	0.3067
Internal Energy (cal/gm)	3016	2802	8899
Slope of V.P. Curve (α)	3.775	4.068	3.745
Parameter β	5.626	5.626	5.638
Zero Pressure Parameters:			
Solid Density (gm/cc)	2.537	4.251	1.732
Liquid Density (gm/cc)	2.380	3.974	1.619
Vapor Density (gm/cc)	2.124×10^{-15}	5.682×10^{-10}	7.079×10^{-9}
Solid Energy (cal/gm)	212.6	279.5	878.3
Liquid Energy (cal/gm)	307.0	356.9	1189
Vapor Energy (cal/gm)	2994	2451	9032

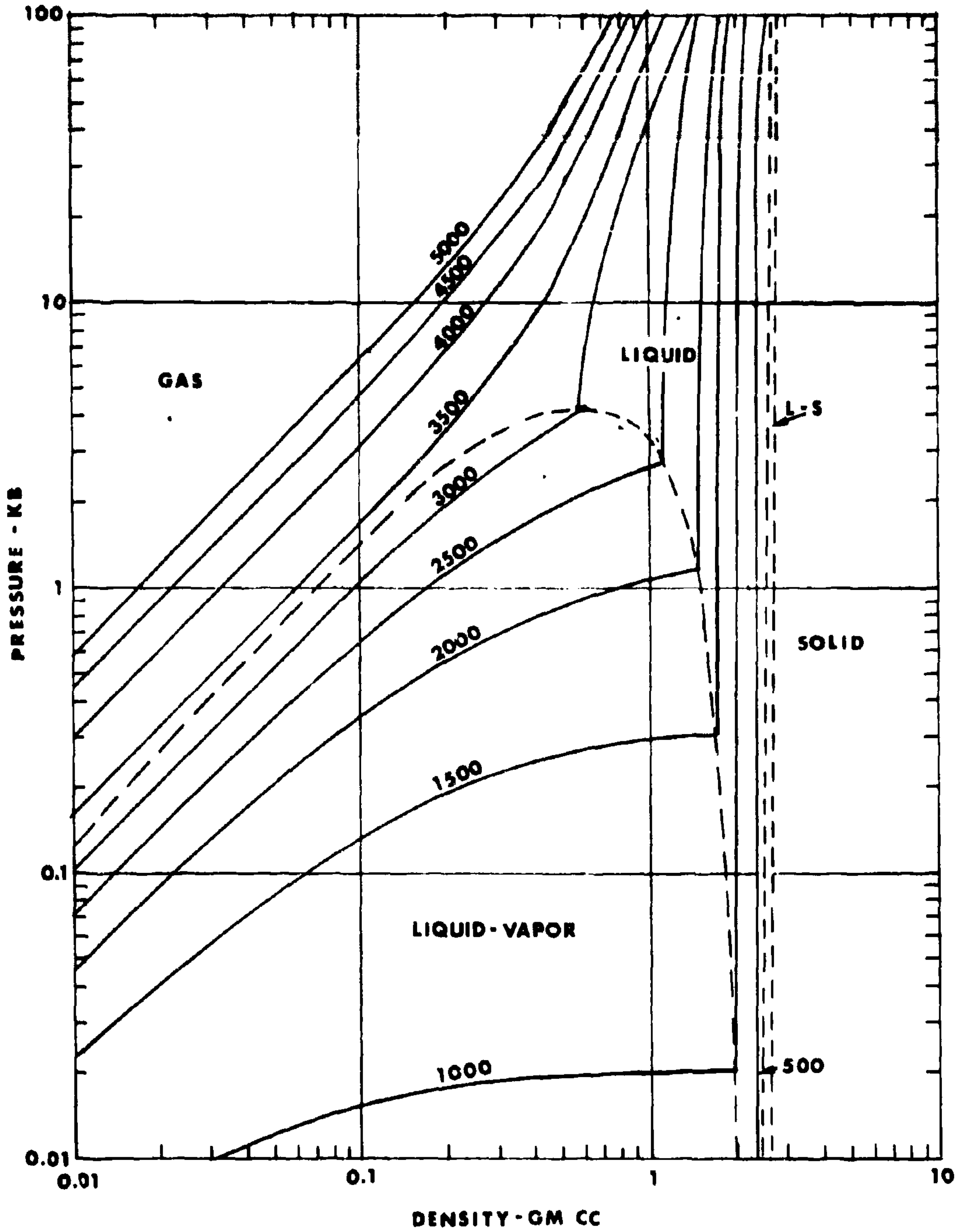

FIGURE 5.1 ALUMINUM ISOENERGY LINES. PARAMETER IS ENERGY IN CAL/GM.

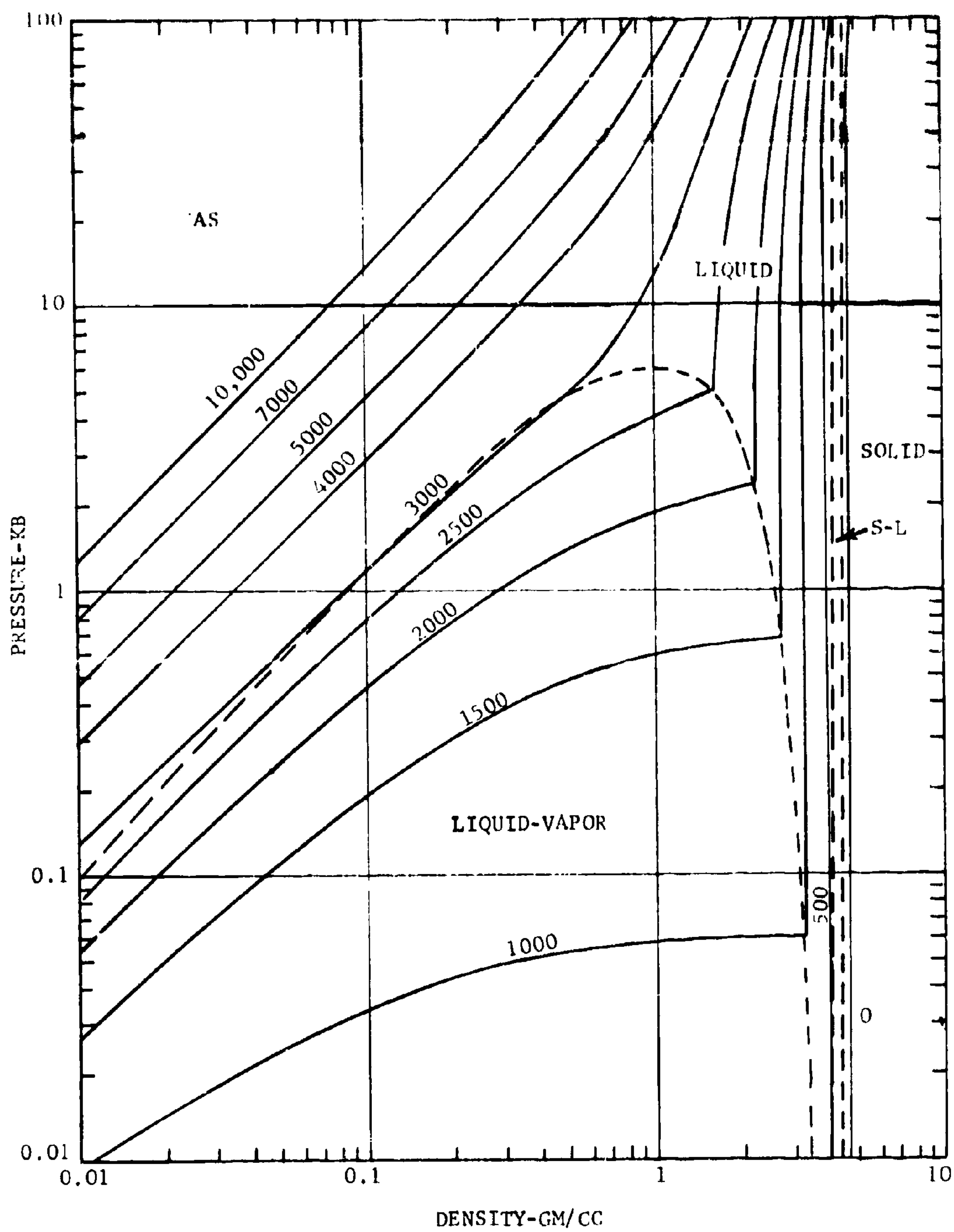

FIGURE 5.2 TITANIUM ISOENERGY LINES. PARAMETER IS ENERGY IN CAL/GM

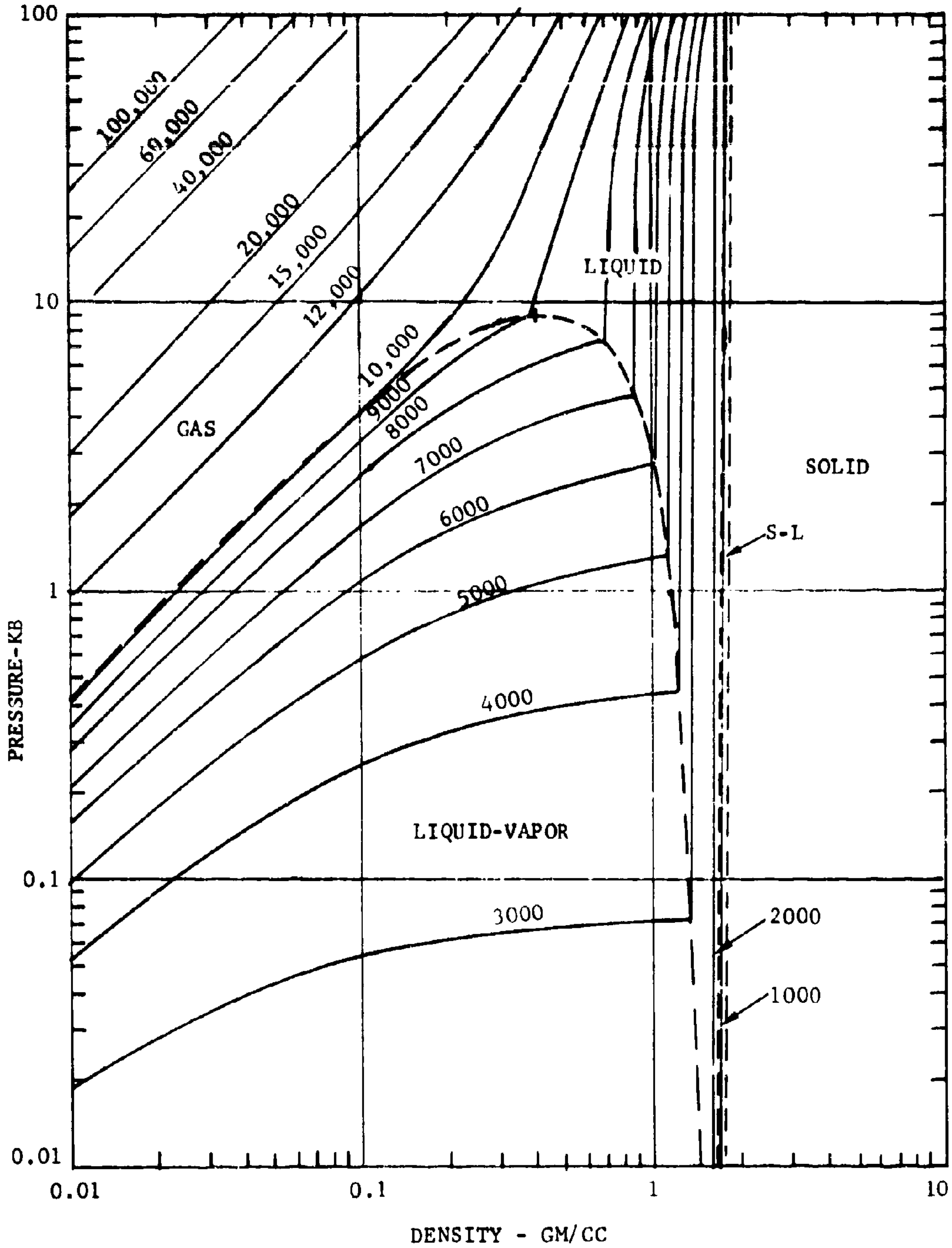

FIGURE 5.3 BERYLLIUM ISOENERGY LINES. PARAMETER IS ENERGY IN CAL/GM.

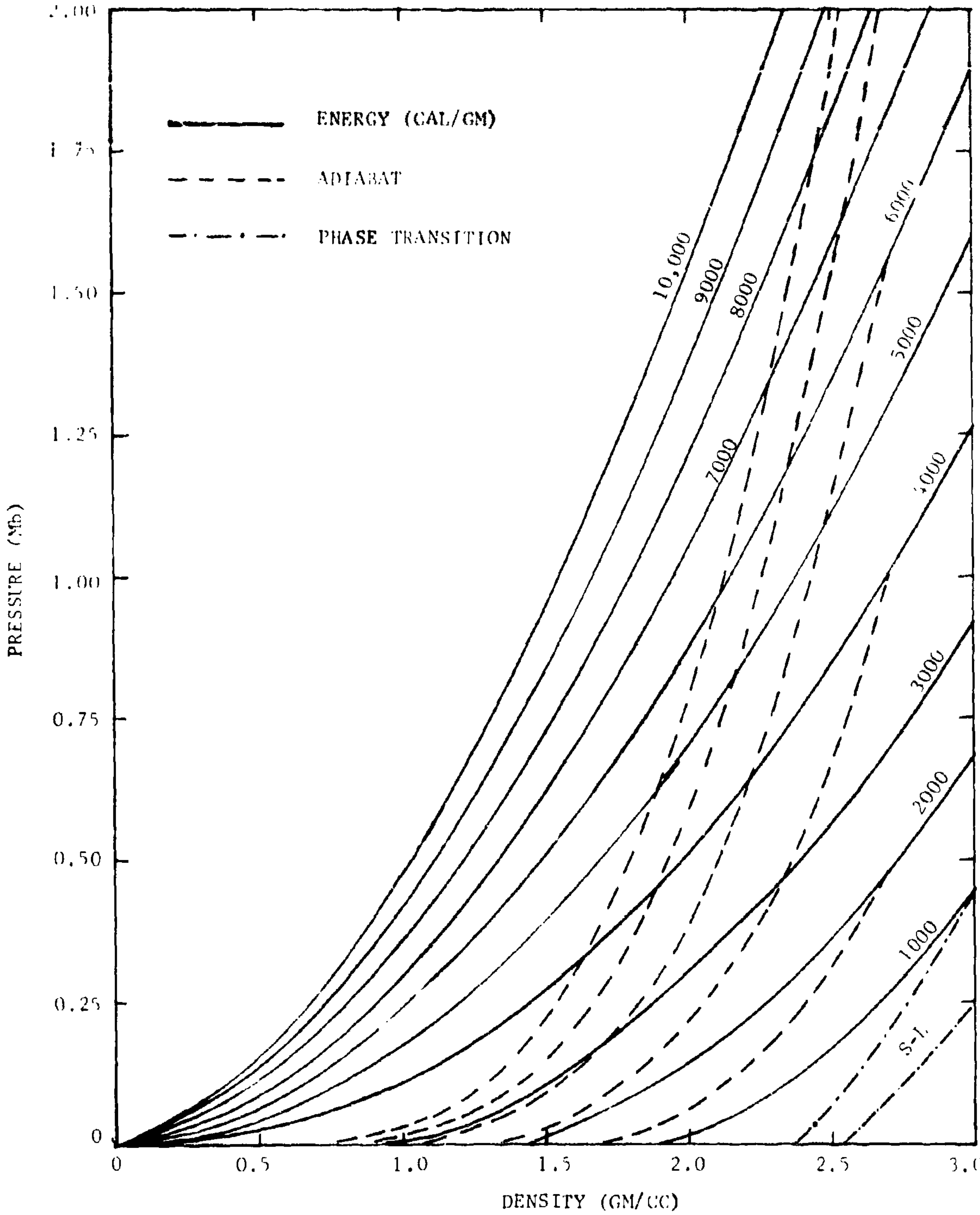

FIGURE 5.4 ALUMINUM ISOENERGY LINES AND ADIABATS

to curves of constant energy, calculated adiabats are also shown. At the high pressures, considerable PdV work is done and hence there is a marked change in internal energy along an adiabat.

Figure 5.5 shows adiabats for aluminum which cut down through the liquid-vapor mixed phase region. At these low pressures there is little distinction between adiabats and curves of constant energy. Provided the formulation is reasonably correct, there are marked breaks in the curves when vaporization begins.

Figure 5.6 is another plot of the adiabats of Figure 5.4 where the internal energy is shown as a function of density. It more clearly indicates the effect of vaporization in an adiabatic process. Although the calculations at very low densities were not made, it is expected that energy recovery proceeds down to the liquid internal energy.

It should be noted that the pressures of Figure 5.4, for a given energy, are about a factor of two higher than those obtained in Ref. 2. This is illustrated in Figure 5.7 which gives the pressure at normal density as a function of internal energy. Also shown is the normal density pressure obtained from the solid equation of state. This is the pressure that most older versions of PUFF would predict for normal density aluminum. The difference is due to the empirical treatments of the so-called liquid phase and, at present, there seems to be no data to support or refute either formulation.

The equation of state program as written is not an efficient program for determining curves of constant energy since it starts from "scratch"

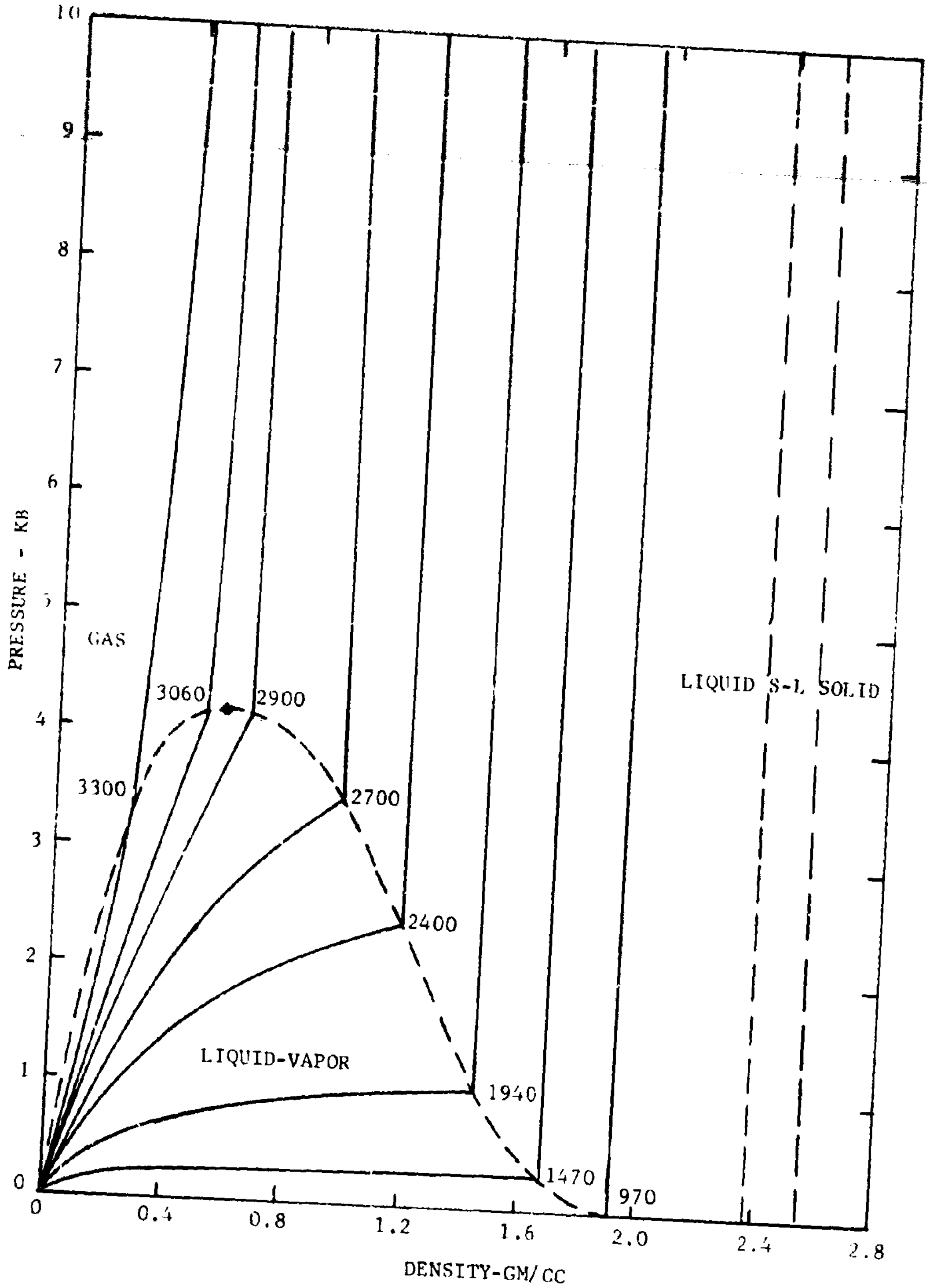

FIGURE 5.5 ALUMINUM ADIABATS. PARAMETER IS ENERGY AT SATURATION BOUNDARY IN CAL/GM

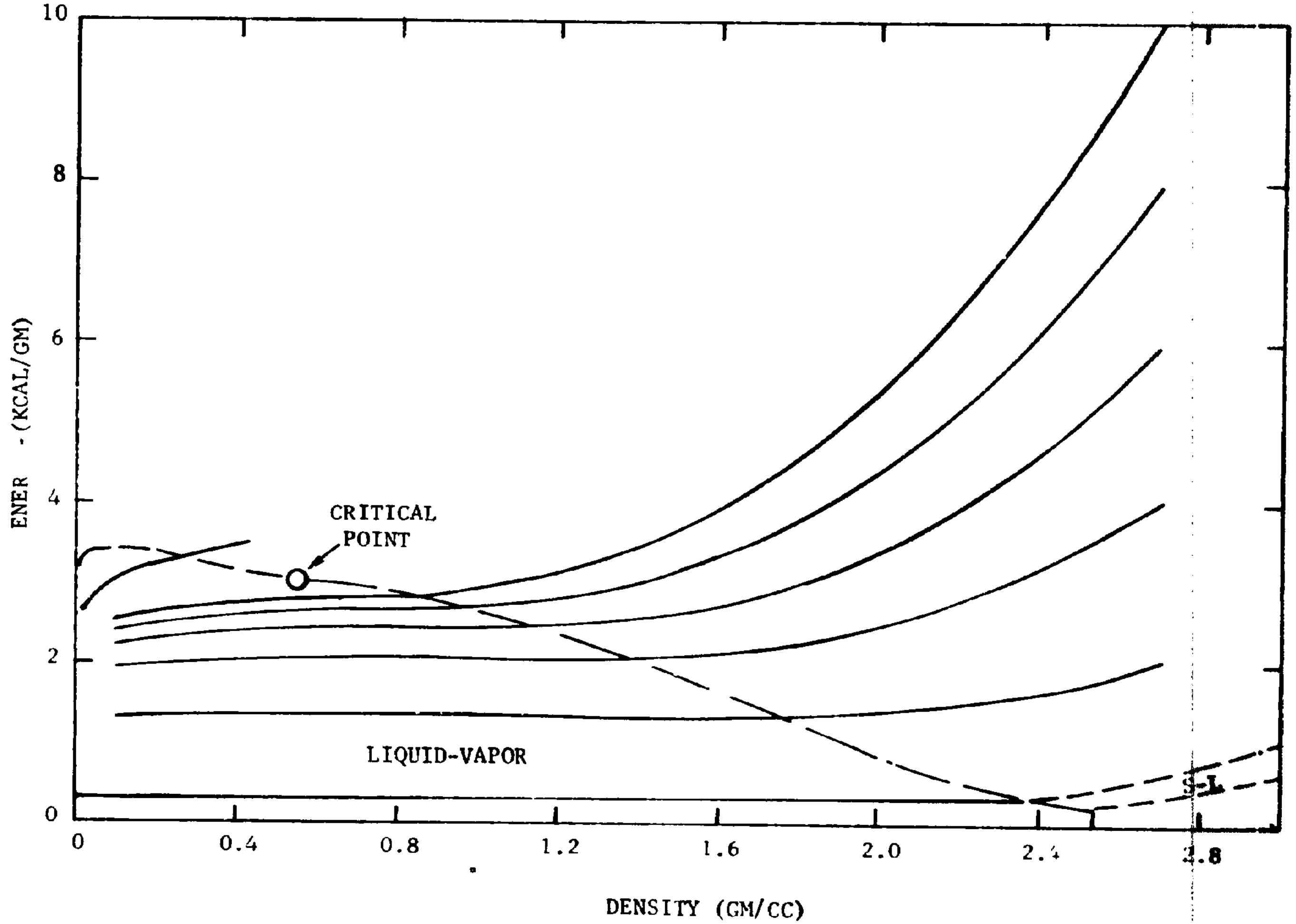

FIGURE 5.6 ALUMINUM ADIABATS SHOWING F RGY RECOVERY

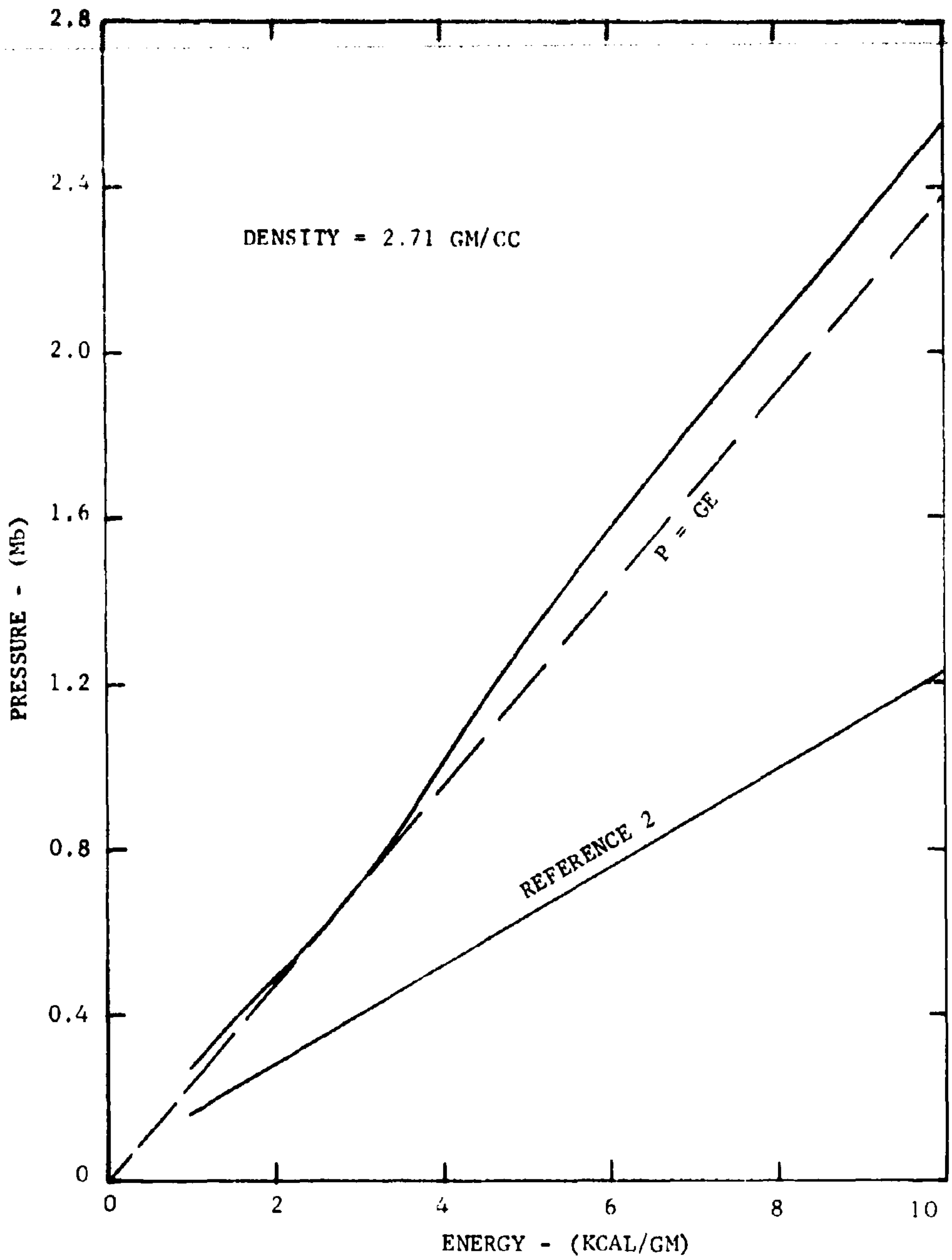

FIGURE 5.7 EQUATION-OF-STATE COMPARISON FOR ALUMINUM AT NORMAL DENSITY

for each pair of values of the volume and energy. If one wished to represent the equation of state in tabular form, as in Ref. 2, a modified program for obtaining these tables should be prepared.

The adiabats were calculated according to the difference equation connecting points 1 and 2,

$$E_2 - E_1 + \frac{P_2 + P_1}{2} (V_2 - V_1) = 0 \tag{5.1}$$

where the iterative process was written into the main program.

All calculations were made on the Aeronutronic Time-Sharing System which utilizes the GE 420 as the main-site computer. A rough estimate of the average time involved to obtain one pressure for a given volume and energy is 0.25 sec. The accuracy imposed on iterations in the subroutine was $10^{-4}\%$.

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SECTION 6

SUMMARY

In summary, two main objectives of the present investigation have been achieved:

1) An analytical model of an equation of state, with phase changes, for pure metals has been developed.

2) An equation of state subroutine which yields the pressure for a given specific volume and energy has been written.

In developing the equation of state model, the effects of dissociation and the possibility of sublimation have been neglected. Hence, at best, it can only apply for pure materials which normally melt and whose vapor consists of atomic species. The lack of data for high temperatures and pressures necessitated many assumptions in order to complete the model and in most cases, plausibility is their only justification.

The data required to determine certain parameters appearing in the formulation are essentially no different from those which have been used in the

past. Now, however, they are used to describe, in a reasonable fashion, the phase changes from solid to liquid and liquid to vapor.

The only metals considered to date have been aluminum, titanium and beryllium. While no difficulties arose for these metals there is no assurance that there isn't some material which will tax the proposed model. A few preliminary calculations for a new material are helpful to check for "reasonability."

Both the equation of state model and the computer subroutine evolved over a period of time. As a result, the program isn't as "clean" as it could be. The main effort was to obtain a workable subroutine and, hence, many of the iterative procedures can undoubtedly be improved.

The numerical results of Section 5 illustrate the type of information that one can obtain with this program. It is noted, however, that the program, as written, gives the pressure for a given volume and energy with no use being made of any prior information concerning the location of the previous point in the phase plane. Therefore, it is quite inefficient, e.g., for obtaining curves of constant energy.

APPENDIX A

CRITICAL POINT MEASUREMENTS USING INERTIAL CONFINEMENT

Above about 2000°C no equation of state measurements in the liquid vapor region have been made using conventional techniques because of the lack of suitable refractory containers and instrumentation. The critical temperature of many metals is well above this conventional technique limit. However, it appears feasible to make measurements at these higher temperatures and pressures by use of inertial confinement for times of the order of microseconds. A number of requirements must be met if this approach is to succeed, the principal one being a means of uniformly heating the test material in a time short compared to the inertial confinement time. There .·e a number of ways in which this might be done.

With such a means of rapidly heating a confined material of less than normal density, the material may be driven almost instantaneously to a pressure above the critical pressure. The material will then expand, compressing the walls containing it. This expansion will be adiabatic if energy losses can be

neglected, so the pressure-density history will follow an adiabat, similar to one of those shown for aluminum in Figure 5.6. The pressure history may be observed, and from it the density history determined. The discontinuity in slope of these observed adiabats at the liquid-vapor saturation envelope serve to locate the envelope, and from it the critical point can be found.

Specifically, a method by which the liquid-vapor region equation of state data may be obtained, utilizing inertial confinement, involves the following steps:

(1) Confine a thin sheet of the material to be investigated between two solid plates of material of sufficient size to make the geometry effectively one dimensional.

(2) Very rapidly heat the confined material uniformly throughout its volume to generate the required pressure.

(3) Minimize container wall heating to reduce background pressures, and to allow use of known cold properties of wall material.

(4) Measure or otherwise determine the specific thermal energy delivered initially to the test material.

(5) Observe the stress wave transmitted to the container wall utilizing a suitable fast response pressure transducer.

(6) Deduce the pressure and density history of the test material using the known dynamic equation of state of the wall material.

(7) Determine the thermal history of the test material from the known

initial specific energy and the approximately adiabatic expansion (corrected for small energy losses).

(8) Locate the liquid-vapor saturation envelope as breaks in the pressure-density traces (adiabats) observed.

(9) Determine the critical point by varying initial conditions to trace out the complete saturation envelope.

Of particular interest at the present time is critical-region data on metals, which have estimated critical pressures up to about 10 Kb, and critical temperatures up to about 10,000°C (e.g., Figures 5.1 to 5.3). The critical densities are less than half of the solid density. To attain these pressure and temperature levels, the almost instantaneous specific energy deposited throughout the volume of material must reach levels of 3000 cal/gm or more. Two methods of heating materials this much, this fast are certain to work. The first is by the use of radiation from a nuclear explosion, and the second is by the use of a Q-switched laser pulse, suitably focused down. The specific energy levels may also be attained by dumping a capacitor (pulsed power) bank and heating the material electrically by use of electron beam pulses, and by use of very high velocity, very thin flyer plates.

Container walls must be of the order of a few millimeters thick to guarantee inertial confinement (i.e., no reflected relief stress wave from outside) for one microsecond. In one-dimensional geometry, the minimum diameter of the heated area must be of the order of a centimeter to avoid edge effects at the center for one microsecond. Also required is a pressure transducer

which can measure many kilobar pressures over a small point only. The laser interferometer transducer recently developed at Sandia[17] has this capability. Others, such as manganan wire transducers may also be adaptable to meet this requirement.

The specific energy deposited may either be calculated from a knowledge of the amount of energy input corrected for losses, or be measured directly by some form of calorimetry or spectroscopy. It is important that the energy be uniformly introduced through the volume of the material, as well as accurately known or measured. For penetrating nuclear radiation no great problem is expected, but for lasers this requirement may prove difficult. Uniformity of energy deposition in either case may be enhanced by using powdered target material to utilize statistical shine-through and multiple scattering.

To make quantitative estimates of feasibility, a particular experiment was considered using lasers to heat aluminum. The pressure transducer chosen was a laser interferometer, and the energy delivered was determined from a knowledge of the input pulse magnitude and energy retention efficiency.

The test material mass is limited by the amount of energy available in a single pulse of a pulsed laser. A typical Q-switched ruby laser can generate a pulse about 50 nanoseconds long, having an energy of about 1 joule, or 1/4 calorie. This limits the mass of material which may be heated to 3000 cal/gm levels to about 0.1 milligram. For a given desired initial density, this in turn limits the test material volume.

The dimensions of the test volume is determined by the interplay of three

factors. The diameter limits the confinement time before edge effects begin. The initial thickness determines the rate of pressure drop due to compression of the chamber walls. Together, the diameter and thickness are pinned to the test volume limit.

Considering these factors simultaneously gave the following values for a 1 gm/cc aluminum target material between fused quartz chamber walls:

Thickness:	9×10^{-4} cm ($\sim$ 0.4 mils)
Diameter:	0.4 cm
Confinement time:	300 nanoseconds

To fix these values, it was required that in the confinement time the volume of the test chamber no more than double.

For these conditions, the pressure pulse profile generated in the fused quartz chamber walls is easily within the measuring capability of a laser velocity transducer. The radiation and conduction losses during the confinement time are of the order of 5 percent, and thus the expansion is nearly adiabatic.

The major problem which must be solved if a laser pulse is used to do the heating is to assure uniform heating of the test material. This appears to be possible in the direction of the laser beam by using powdered aluminum particles of appropriate size (of the order of microns). Based on turbid medium theory,[18] target absorptions approaching 50 percent are possible even for highly reflecting particles because of multiple scattering, and at the same time the distribution in depth is kept reasonably uniform.

The use of a pulsed laser to obtain valuable equation-of-state data near the critical point appears feasible. This technique may be traded-off against other approaches to find the most promising one. Obtaining equation-of-state data by one of the inertial confinement approaches will make possible location of critical points for metals and refractory materials, and clarify the form of their equations of state in the liquid and liquid-vapor regions.

APPENDIX B

RELATION BETWEEN STRESS AND PRESSURE

In general, the value of Poisson's ratio ν for a solid is different from 1/2 and hence, in an idealized one-dimensional propagation problem, the stresses normal to and parallel to the direction of propagation are different. This is not the case for liquids and vapors where $\nu = 1/2$. Since the material motion is governed by the gradient of the stress in the direction of propagation, it is desirable to obtain a relation between this stress and the so-called hydrostatic pressure used throughout the equation of state formulation.

The theory of thermal stress analysis, in the limit of small strains, is well known[19,20] and, for a strain ε only in one direction, the stresses parallel (σ) and normal (σ_n) to this direction are

$$\sigma = 3 \frac{1 - \nu}{1 + \nu} K \varepsilon - K \alpha_v T, \tag{B.1a}$$

$$\sigma_n = \frac{3\nu}{1 + \nu} K \varepsilon - K \alpha_v T. \tag{B.1b}$$

The usual convention of a stress being positive in tension has been used. The various quantities appearing are Poisson's ratio ν, the bulk modulus K, and the volume coefficient of thermal expansion α_v. When $\nu = 1/2$, the coefficients of the strain are both equal to 1 and there is no difference in the stresses.

The pressure is now defined by

$$P = - \frac{\sigma + 2\sigma_n}{3} = - K \epsilon + K \alpha_v T = K \frac{V - V_o}{V_o} + K \alpha_v T. \qquad (B.2)$$

The thermal expansion term of this expression is associated with the internal energy term of Eq. (3.35) and hence,

$$K \alpha_v T \rightarrow G(\eta)E. \qquad (B.3)$$

Eliminating the strain between Eqs. (B.1a) and B.2) and making the substitution of Eq. (B.3) yields

$$\sigma = -2 \frac{1 - \nu}{1 + \nu} P + 2 \frac{1 - 2\nu}{1 + \nu} G(\eta)E \qquad (B.4)$$

where σ is still positive in tension. For $\nu = 1/2$, $\sigma = - P$, as it should.

Eq. (B.4) is suggested as the proper relation between the pressure of the equation of state formulation and the stress which determines material motions whenever this difference is taken into account.

APPENDIX C

EQUATION OF STATE SUBROUTINE LISTING

Section 4 summarizes the equations incorporated into the equation of state subroutine, enumerates the calculations necessary to determine certain parameters and to define boundaries in the phase plane, and indicates a possible checking procedure. It also lists the required input data with units which must be made available to the program.

Following is a listing of the program which determines the pressure in kbar for a given volume in cc/gm and energy in cal/gm. The program is written in Fortran IV for a time-share system. It may be easily adapted to Fortran IV for other computers.

EQST SUBROUTINE

```
C     EQUATIØN ØF STATE SUBRØUTINE, P(V,E)
      FUNCTIØN P(V,E)
      CØMMØN WT,DO,TCK,C1,D1,KO,TMK,HSM,HLM,HVM,DSM,DLM,TCK,HLB,PV
      CØMMØN C,D,S,G ,INIT
       REAL INIT,KO,K1,K2,LB,MU
      FF(MU) = MU*MU*(D+S*MU)
      GG(ETA) = G*ETA
      FFP(MU) = (D+D+3.*S*MU)*MU
      GGP(ETA) = G
       IF(INIT)111,800,111
C  INITIAL ØNCE-ØNLY CALCULATIØNS
  800 ACC = 1E-6
      R1 = 1.98726
      R2 = .0820597
      V0 = 1./D0
      IF(DSM) 1,1,2
    1 ESO = HSM*1E3/WT
      EPSO = ESO
       TF=1.
      EOVO = 0
      ETA = 1.
      ASSIGN 8051 TØ JSO
      GØ TØ 8000
 8051 VSO = VS
      DSO = 1./VS
      GØ TØ 3
    2 DSO = DSM
      ETA = DSO/DO
      MU = ETA-1.
      ESO = -(C*MU+FF(MU))/GG(ETA)
      VSO = 1./DSO
    3 ELO = ESO+1E3*(HLM-HSM)/WT
      IF(DLM)4,4,5
    4 DLO = .935*DSO
      GØ TØ 6
    5 DLO = DLM
    6 VLO = 1./DLO
      TM = TMK/TCK
      TE = TMK/TCK
      LB = 1E3*(HVB-HLB)
```

```
      CL = 1E3*(HLB-HLM)/(T3K-TMK)
      CV = 1E3*(HVB-HVM)/(T3K-TMK)
      DLTC = CV-CL
      A2 = (LB-DLTC*TBK)/(R1*TCK)
      A1 = DLTC/R1
      ALPHA = A2+A1
      X = 36./TB+5.*TB**6-42.
      AR = (A2/TB+A1+.31425*X)/(1.+.0938*X)
      ZC = 1./(3.72+.26*(AR-7.))
      ROOT3 =1./3.
      RL = 1.+C1*(1.-TM)**ROOT3+D1*(1.-TM)
      DC = DLO/RL
      VC =1./DC
      PC = ZC*R2*TCK*DC/WT
      B1 = 3.
    7 B0 = B1
      B1 = 3.*(1./ZC-1.)-(1./ZC+3.+1./B0)/B0
      IF(ABS((B1-B0)/B1)-ACC) 8,8,7
    8 B = ((3.*B1-6.)*B1-1.)/(B1*(3.*B1-1.))
      BP = (B1-3.)/(3.*B1-1.)
      IF(K0) 10,9,10
    9 K0 = B1
   10 K1 = B1-K0
      K2 = (1.+K1+B1-ALPHA)/2.
      EPS1 = ZC*R1*TCK/WT
      EPS2 = TCK*(CV-R1)/WT
      E0 = (1E3*HVB-CV*T3K)/WT
      T = TM
      ASSIGN 9051 TØ J90
      GØ TØ 9000
 9051 E1 = E0+EL0-EL
      EV0 = EV+E1-E0
      PV0 = PV
      DV0 = DC*RV
      VV0 = 1./DV0
      E0 = E1
      EC = E0+EPS2-EPS1*(K0+K1+K1-K2)
      DLTE0 = EL0-ES0
      EE = 4.*ES0*DLTE0
      DLTV0 = VL0-VS0
      DEDV = DLTE0/DLTV0
      E0V0 = .041293*DLTE0/DLTV0
      EES = V0*DEDV
      EET = E0V0*EES/ES0
      EDV = ES0*DLTV0
       CC=((C1/D1)**3)/27
       CS0=1E3*HSM/(WT*(TMK-298.))
       CL0=CL/WT
       C3=(CL0+CS0)/2.
       DLTC0=CL0-CS0
       DCT=DLTC0*TMK
```

```
      HDCT=DCT/2.
      CBT=C. *TMK
      ELB=ELO-CSO*TMK
      ESB=ESO-CLO*TMK
      Y1=2.*CBT
      Y3=Y1*DCT
      INIT=1
C     END ØF INITIAL CALCULATIØNS
C GIVEN V,E: FIND REGIØN ØF PHASE DIAGRAM
111 IF(E-ESO) 150,150,112
 112IF(V-VLO)130,134,139
130 GØ TØ 4000
4051 IF(V-VS)150,150,131
131 IF(E-ELO) 132,132,134
132 FMAX = (E-ESO)/(ELO-ESO)
      VMAXE = FMAX*VLO+(1.-FMAX)*VSO
      IF(VMAXE-V)984,984,133
984 P = 0.
      GØ TØ 9998
133 GØ TØ 4500
4551GØ TØ 160
134 GØ TØ 5000
5051 IF(V-VLM)133,160,135
135 IF(E-EC)136,137,138
136 GØ TØ 5500
5551 GØ TØ 170
137 VLB = VC
      PLB = PC*(1.-PVO)
      GØ TØ 170
138 GØ TØ 6000
6051 GØ TØ 170
139 IF(E-ELO)132,132,140
140 IF(V-VC)141,144,146
141 GØ TØ 6500
6551 IF(E-ELB)142,180,134
142 GØ TØ 7000
7051 GØ TØ 130
144 ELB = EC
      PV = 1.
      T = 1.
      IF(E-EC)142,180,190
146 IF(V-VVO)147,190,190
147 GØ TØ 7500
7551 IF(E-EV)142,180,190
C END ØF PHASE LØCATIØN
C SØLID PHASE P(V,E)
150 ETA = VO/V
      MU = ETA-1.
      P = C*MU+FF(MU)+GG(ETA)*E
      GØ TØ 9998
C SØLID-LIQUID MIXED PHASE P(V,E)
```

```
  160 P = E0V0*(TF-1.)
      GØ TØ 9998
C LIQUID PHASE P(V,E)
  170 RM=1./VLM
      RB=1./VLB
      Z1=(PLM-PLB)/(RM-RB)
      Z2=(RB*PLM-RM*PLB)/(RM-RB)
      P1=Z1/V-Z2
      Z3=ALØG(PLM/PLB)/ALØG(RM/RB)
      Z4=(ALØG(RB)*ALØG(PLM)-ALØG(RM)*ALØG(PLB))/ALØG(RM/RB)
      ALP2=Z3*ALØG(1./V)-Z4
      F=(PLM/(RM-BLB)-Z3*PLM/RM)/(Z1-Z3*PLM/RM)
      IF(F)171,174,172
  171 F=0
      GØ TØ 174
  172 IF(F-1.)174,174,173
  173 F=1.
      GØ TØ 174
  174 P=EXP(F*ALØG(P1)+(1.-F)*ALP2)
      GØ TØ 9998
C LIQUID-VAPOR MIXED PHASE P(V,E)
  180 P = PC*(PV-PV0)
      GØ TØ 9998
C VAPOR PHASE P(V,E)
  190 RV = VC/V
      ASSIGN 8551 TØ J85
      GØ TØ 8500
 8551 P = PC*PG
      GØ TØ 9998
C BEGIN SUBRØUTINES
C GIVEN ES0<E; FIND VS(E)
 4000 Y2=E-EBS
      TF=(Y2+SQRT(Y2*Y2-Y3))/Y1
      ETA=1.
      EPS0 = E
      ASSIGN 3052 TØ J30
      GØ TØ 3000
 3052 GØ TØ 4051
C GIVEN V,E IN S-L REGIØN; FIND T(V,E)
 4500 EPS=E-DEDV*V
      ES=EPS+DEDV*VS
      Y2=ES-EBS
      TF=(Y2+SQRT(Y2*Y2-Y3))/Y1
 4501 TF0=TF
      ETA=V0/VS
      MU=ETA-1.
      ESP=CBT-HDCT/(TF*TF)
      ETAP=-ESP*ETA*ETA/EES
      H=E0V0*(TF-1.)-C*MU-FF(MU)-GG(ETA)*ES
      HP=E0V0-(C+FFP(MU)+GGP(ETA)*ES)*ETAP-GG(ETA)*ESP
      TF=TF-H/HP
```

```
      ES=EBS+CBT*TF+HDCT/TF
      VS=(ES-EPS)/DEDV
      IF(ABS((TF-TFO)/TF)-ACC)4502,4502,4501
 4502 GØ TØ 4551
C GIVEN ELO<E: FIND VLM(E),PLM(E)
 5000 Y2=E-EBL
      TF=(Y2+SQRT(Y2*Y2-Y3))/Y1
      ES=EBS+CBT*TF+HDCT/TF
      ETA=1.
      EPSO = ES
      ASSIGN 8053 TØ J80
      GØ TØ 8000
 8053 VLM=VS+(E-ES)/DEDV
      PLM=PS
      GØ TØ 5051
C GIVEN ELO<E<EC: FIND VLB(E),PLB(E)
 5500 TL = TM
      TU = 1.
 5501 T = (TL+TU)/2.
      ASSIGN 9052 TØ J90
      GØ TØ 9000
 9052 IF(ABS((E-EL)/E)-ACC)5505,5505,5502
 5502 IF(E-EL)5503,5505,5504
 5503 TU = T
      GØ TØ 5501
 5504 TL = T
      GØ TØ 5501
 5505 VLB = VC/RL
     PLB = PC*(PV-PVO)
      GØ TØ 5551
C GIVEN EC<E: FIND VLB = VC,PLB(E)
 6000 VLB = VC
      RV = 1.
      ASSIGN 8552 TØ J85
      GØ TØ 8500
 8552 PLB = PC*PG
      GØ TØ 6051
C GIVEN VLO<V<VC: FIND ELB(V)
 6500 RL = VC/V
      X1 = (1.-RL)/D1
      X = SQRT(X1*X1/4.+CC)
      X2 = (X-X1/2.)**RØØT3
      X3 = -(X+X1/2.)**RØØT3
      Y = X2+X3
      T = 1.-Y**3
      ASSIGN 9053 TØ J90
      GØ TØ 9000
 9053 ELB = EL
      GØ TØ 6551
C GIVEN V,E IN L-V REGIØN; FIND T(V,E),PV(T)
 7000 R = VC/V
```

```
      IL = IM
      TU = T
      FMAX = (E-ELO)/(EVO-ELO)
      VMAXE = FMAX*VVO+(1.-FMAX)*VLO
      IF(V-VMAXE)7001,7010,7010
 7010 P = 0.
      GO TO 9998
 7001 T = (TL+TU)/2.
      ASSIGN 9054 TO J90
      GO TO 9000
 9054 F = (1./R-1./RL)/(1./RV-1./RL)
      ET = F*EV+(1.-F)*EL
      IF(ABS((E-ET)/E)-ACC)7005,7005,7002
 7002 IF(E-ET)7003,7005,7004
 7003 TU = T
      GO TO 7001
 7004 TL = T
      GO TO 7001
 7005 GO TO 7051
C GIVEN VC<V<VVO; FIND EV(V)
 7500 RV = VC/V
      X1 = RV/(ZC*(1.-(B-BP*RV)*RV))-K2*RV**3
      X2 = -K0*RV*RV
      X3=(K2*RV-K1)*RV*RV
      T=1.
      PV = EXP(A2*(1.-1./T)+A1*ALØG(T))
 7501 PVT = PV
      TO = T
      PG = X1*T+X2+X3/T
      PVP = PV*(A2/T+A1)/T
      PGP = X1-X3/(T*T)
      T=TO+(PG-PV)/(PVP-PGP)
      PV = EXP(A2*(1.-1./T)+A1*ALØG(T))
      IF(ABS((PV-PVT)/PV)-ACC)7502,7502,7501
 7502 EV = E0+EPS2*T-EPS1*((K0+2.*K1/T)-K2*RV/T)*RV
      GO TO 7551
C GIVEN ES0<EPS0; FIND VS(EPS0)
 8000 PS=E0VO*(TF-1.)
 8001 ETA0 = ETA
      MU = ETA -1.
      X = C*MU+FF(MU)+GP(ETA)*EPS0
      XP = C+FFP(MU)+GPP(ETA)*EPS0
      ETA = ETA0+(PS-X)/XP
      IF(ABS((ETA-ETA0)/ETA)-ACC)8002,8002,8001
 8002 VS = V0/ETA
      GO TO J80,(8051,8052,8053)
C GIVEN V,E IN VAPOR PHASE; FIND PG(V,E)
 8500 X1 = E-E0+EPS1*K0*RV
      X2 = EPS1*(K2*RV-2.*K1)*RV
      T = (X1+SQRT(X1*X1-4.*EPS2*X2))/(2.*EPS2)
      PG=RV*T/(ZC*(1.-(B-BP*RV)*RV))-(K0+K1/T+K2*(T-1./T)*RV)
```

```
&         *RV*RV-RV)
          GO TO J55,(9551,9552)
C GIVEN T<1: FIND PV,RV,EV,RL,EL OF T
     9000 GO TO 9500
     9551 RL = 1.+C1*(1.-T)**R0T3+D1*(1.-T)
          EL = EV-EPS1*PV*(1./RV-1./RL)*(A2/T+A1-1.)
          GO TO J90,(9051,9052,9053,9054)
C GIVEN T>1: FIND PV,RV,EV OF T
     9500 PV = EXP(A2*(1.-1./T)+A1*ALOG(T))
          X1 = T/ZC
          A = K0+K1/T
          AP = K2*(T-1./T)
          RV = PV/X1
     9501 RV1 = RV
          X2 = 1.-(B-BP*RV)*RV
          P0 = X1*RV1/X2-(A+AP*RV1)*RV1**2
          P0P = X1/X2+(X1*RV1*(B-2.*BP*RV1))/(X2*X2)
&         -(2.*A+3.*AP*RV1)*RV1
          RV = RV1+(PV-P0)/P0P
          IF(ABS((RV-RV1)/RV)-ACC)9502,9502,9501
     9502 EV = E0+EPS2*T-EPS1*((K0+2.*K1/T)-K2*RV/T)*RV
          GO TO 9551
     9998 RETURN
          END
```

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13. ABSTRACT

An equation of state model, including the solid to liquid and liquid to vapor phase transitions, has been developed. It is applicable for materials which usually melt, rather than sublimate, and whose vapor consists of atomic species. The parameters appearing in the formulation are completely determined from a limited amount of data which, for many materials, is currently available. A computer program which gives the pressure as a function of volume and internal energy has been written and used to obtain numerical results for aluminum, titanium, and beryllium.

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~~Equation of State~~						
Phase Changes						

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